

# Modeling of Particulate Systems

# Contents

<b>Preface</b>	<b>iii</b>
<b>1 Introduction</b>	<b>1</b>
1.1 What is Process Modeling and Simulation . . . . .	1
1.2 Basics of modeling . . . . .	2
1.3 Modeling of a unsteady state CSTR . . . . .	3
1.4 Preparing an information flow diagram . . . . .	4
1.5 What are particulate systems? . . . . .	4
<b>2 Modeling of a crystallizer</b>	<b>7</b>
2.1 Fundamental Concepts . . . . .	7
2.1.1 Particle State Vector . . . . .	7
2.1.2 Representation of a population of particles . . . . .	9
2.2 A Batch Cooling Crystallizer . . . . .	11
2.2.1 Understanding the problem . . . . .	11
2.2.2 Population balance equation for pure growth . . . . .	12
2.2.3 Coupling the PBE with mass balance . . . . .	14
2.2.4 Nucleation . . . . .	14
2.3 Number balance for open system . . . . .	15
2.4 Exercise . . . . .	16
<b>3 The process of breakage</b>	<b>23</b>
3.1 The physics of the breakage process . . . . .	24
3.2 Number balance for breakage . . . . .	26
3.2.1 Required properties of the daughter distribution function	27
3.3 Discrete breakage equation . . . . .	27
3.4 Exercise . . . . .	28

<b>4</b>	<b>Aggregation process</b>	<b>33</b>
4.1	Number balance for aggregation . . . . .	34
4.2	Estimation of aggregation frequency . . . . .	38
4.3	Exercise . . . . .	38
<b>5</b>	<b>Solution of population balance equation</b>	<b>47</b>
5.1	Operations involving moments of the PBE . . . . .	48
5.2	analytical solution of PBE . . . . .	50
5.2.1	Solution of growth equation: method of characteristics	50
5.2.2	Solution of aggregation equation: method of Laplace transforms . . . . .	51
5.2.3	Solution of breakage equations: similarity analysis . . .	54
5.3	Numerical Solution of population balance equation . . . . .	56
5.3.1	discretization of the breakage equation . . . . .	56
5.4	Exercise . . . . .	59
<b>6</b>	<b>Kinetic Monte Carlo Simulation</b>	<b>63</b>
6.1	Random variables and Distribution Functions . . . . .	63
6.1.1	Examples of random variables and its distribution func- tion . . . . .	64
6.2	Random numbers and Pseudo-random numbers . . . . .	65
6.3	Mean field versus stochastic model . . . . .	65
6.4	Kinetic Monte Carlo . . . . .	66
6.4.1	Selection of system size . . . . .	66
6.4.2	Interval of Quiescence (IQ) . . . . .	67

# Chapter 1

## Introduction

### 1.1 What is Process Modeling and Simulation

What is a process. A process is a process! for example, distillation is a process, crystallization is a process, humidification is a process, drying is a process.

What is modeling. Often, we want to know certain things about a process. For example, what is the 'rating' of a pump for a certain flow of liquid across a packed bed? The tools that one can use to answer such questions (of course one can buy 100 pumps of a variety of capacity and test those one by one until it fits the requirements, then we can try return those 99 pumps to the manufacturer to get back the extra money) but the better and easy way is to use Ergun equation and estimate what could be the possible pressure drop and then select 2-3 pumps based on that. The ergun equation tells you the pressure drop across an existing packed bed if you give certain input regarding the porosity of the bed, superficial velocity (which you can obtain from the volumetric flow rate required and the dia of the vessel). Hence, **ergun equation is a model equation for the packed bed. It represents the bed quantitatively.** i.e. it not only tells you that 'increase in flow rate will increase pressure drop' but gives you the precise number that how much will be the pressure drop for a given flow rate. This is a model. How good is the number provided from the model? how well it matches the observation? That depends on the goodness of the model and the complexity of the system. Some model can only predict the order of magnitude. Some model, developed

for an well known systems may be able to produce a precise number.

Sometimes instead of a thorough understanding of the system, a set of observations around a black box is available. those data follow a particular trend which may be represented by an equation. Such an equation is called an empirical model.

What is a simulation. **Simulation is the process of obtaining numbers from the model.** For ergun equation, it is easy: just put the numbers. For other cases, it may be farely complex to call it by such a fancy name. It often involves solving a set of ordinary or partial differential equations. For example, solving NS equations for flow modeling.:w

## 1.2 Basics of modeling

How to develop the model? Apart from empirical model, there are a set way in which a model is developed. According to \*\*, there are seven basic steps to develop a model:

- Understand the system **as fine grain as possible**. Ask a lot of how and why.
- List **all questions that should be answered** by the model.
- Write down the **precise quantities** you want your model to answer.
- Represent the system by a **simpler one keeping the key features**.
- Write down **all balance equations** (mass balance, heat balance, momentum balance, population balance)
- Write down **all constitutive equations**
- Check **whether it formed a closed set of equations** that can be solved
- Make **suitable assumptions if the set is not closed**. Assumptions should be justified, verifiable and consistent.
- **Solve** the set of equations.
- look back: is it representing the system? check for physical reality of the results, **check for limiting cases**.

## 1.3 Modeling of a unsteady state CSTR

Consider a CSTR as shown in the figure below. We want to model this system. Because chemical engineers spend a lot of time in understanding the system, we can skip step 1 presently and directly go to step 2. What is being asked? Possibly, the manager (the ultimate goal of the modeler in these lectures is to please the manager) wants to know how the concentration of A and B varies with time and what steady state value they reach. The quantities we are interested in is therefore  $C_A(t)$  and  $C_B(t)$ . The system is well mixed and isothermal. Hence heat balance is not required. The mass balance can be written. The system has three species: A, B and the solvent. Hence, three mass balances can be written. The rate of the reaction should also be known. Let us consider, that the rate of the reaction is given by:

$$-r_A = kC_A \quad (1.1)$$

The three mass balance equations now can be written as: (we are writing mol balance and volume balance respectively. why?)

$$\frac{d[V_R C_A]}{dt} = F_{in} C_{Ain} - F_{out} C_A + r_A V_R \quad (1.2)$$

$$\frac{d[V_R C_B]}{dt} = -F_{out} C_B - r_B V_R \quad (1.3)$$

$$\frac{dV_R}{dt} = F_{in} - F_{out} \quad (1.4)$$

We need another equation that comes from momentum balance. The outflow is dependent on the height of the liquid in the tank and this can be written as

$$k\sqrt{h\rho g} = F_{out} \quad (1.5)$$

Now, these set of equations can be solved to obtain the  $C_A$  and  $C_B$ . Now, if the reactor, instead of being a single phase one, be small oil drops? (which actually happens in emulsion polymerization. and emulsion polymerization is inevitable because it produces very high molecular weight polymers). Surely, the set of equations will be changed. How will they change? If we look back we could see that in this case, the continuous system can be seen as a set of batch reactor of a variety of sizes that are residing in the reactor environment for residence time according to the rtd of the CSTR which is

known. **This is a particulate system.** This system surely cannot be modeled using heat mass and momentum balance equation alone and a 'number balance equation' must be written for this case.

## 1.4 Preparing an information flow diagram

## 1.5 What are particulate systems?

Particle technology finds application in liquid liquid dispersion, breakage of particles, crystallization, polymerization etc. Particulate systems contribute to a major part of engineering. Many products are sold as particles in various forms. For example, the most of the drugs that we take are in form of powder, pressed in the form of tablet. The buildings are made from cement which is also particle, many medicine and beauty products are sold as dispersions. For most of the industrial products particulate systems are involved in some or other step of its production. That is the reason why particulate system engineering is very important. Industries are paying more and more attention towards engineering understanding of such systems (what is engineering understanding?)

Name of different product sold as particles:

- detergents
- aftershaves
- medicines
- polymers
- cements

The particles are always dispersed in a medium. At least for all practical cases. The colloidal system, all sorts of particles are found to be dispersed in a medium:

-	s	l	g
l	sol	Emulsion	Foam
g	Pollen	Cloud	
s	Wood	Oil-rock	Pumice Stone

In the next chapter we will see how we model such systems.

# Bibliography

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# Chapter 2

## Modeling of a crystallizer

Crystallizer is a typical chemical engineering system that must be modeled by using concepts of particulate system. In this chapter we shall model a crystallizer. However, before we plunge into modeling of crystallizer, let us understand a few basic ideas of particulate system modeling. Like the concept of molar concentration, i.e. the number (in terms of moles) of molecules of a certain kind per unit volume of the reactor is central to modeling of a reactor, there are several key concepts for particulate system modeling.

### 2.1 Fundamental Concepts

#### 2.1.1 Particle State Vector

##### Internal coordinates

In a reacting system the identity of a species is defined by its molecular weight or atomic or molecular structure. Similarly, in a particulate system, an individual particle can be identified by one or more number of variables. The set of variables that are required to identify a particle uniquely are called its state variable. One important distinction between molecular and particulate system is that each molecule of a species are identical to another (at least for majority of the cases) but particles do differ substantially from one another. For example, if benzene is dispersed in aqueous phase, it forms nearly spherical drops. Each drop has identical composition (pure benzene) and can be considered to be perfect sphere (at least as an idealization). But the size of the drops vary over several orders of magnitude. Hence an

individual drop of benzene may be identified by its size, mathematically the state variable is the diameter of the drop. This variable, that describe a particle uniquely among a population of particles is called its "internal state variable" or "internal coordinate." This is something like your first name. A name is attached to an individual in a population. For example, 'Naman'.

Now, if drops of benzene and toluene are mixed in a vessel, where benzene particles and toluene particles coalesce and re-disperse, the composition of particles will vary. There may be some pure benzene particle which by chance escaped collision with toluene particles, some pure toluene particle may also be there and surely there will be many particles which have both benzene and toluene in it. Now, will diameter suffice to specify this particle completely? Surely not. Because, particles with the same size may have different composition! Hence, to describe the a drop uniquely, we must specify the mass fraction of benzene (or toluene) in the particle along with its diameter. This will complete the description and any two particles with the same diameter and mass fraction of benzene are indistinguishable.

In a population of students this is similar to having two students having the same name! If you have two students named Naman, we resort to their family name to distinguish them. For example, 'Naman Thakur' and 'Naman Jain' now identify them completely. In this case, only one internal coordinate is not sufficient and two quantities are needed. These two quantities can be written in a vector like  $[dx]$  or [name surname] and is called "internal coordinate vector". Internal coordinate vectors need not to have only two elements. It can have any number of elements necessary to describe a particle/drop uniquely. For example, if the particles are cells and a set of protein identify a cell uniquely, it is the vector giving the concentration of each protein. The internal coordinate vector will be represented by the symbol  $\mathbf{x}$

### External Coordinate

Internal coordinates are something inherent to the particle. No matter where the particles go, they carry that identity. That is why it is called internal coordinate. (Like Naman Jain is Naman Jain in all classes: he is not called 'Ravi Thakur' in Fluid mechanics class and 'Mani Rattan' in Mass Transfer Lab). But the location of the particle changes in a particulate system due to movement of the fluid they are suspended in and the location of a particle at any particular instant is sometimes important. In other words, the 'current

coordinate' of a particle (You can probably track the current co-ordinate of your friend in Google or Facebook!) is important. The xyz coordinate of a particle is called its external coordinate.

Sometimes the behavior of particles of same internal coordinate (say particles of same diameter and composition) may be different depending on its external coordinate. The environment may be different at different positions and in certain positions temperature may be sufficiently high to allow degradation of toluene to produce another compound. Hence in some cases, where the environment is not uniform, the location of particle needed to be specified. The location is clearly given by a vector composed of the x y and z coordinates of the particle. This is the "external coordinate vector". The external coordinate vector is denoted by the symbol  $\mathbf{r} = [xyz]$

The complete description of a particle is therefore given by a combined vector of internal and external coordinates, which is called the "particle state vector".

### Continuous phase vector

The particles are usually suspended in a fluid. The fluid in which the particulate phase is suspended is called the continuous phase. For example, crystals are suspended in the mother liquor. In this case, the mother liquor is the continuous phase. The condition of the mother liquor determines the growth of the crystals and hence the properties of the continuous phase is also an important variable. In some cases, only one property (e.g. concentration) of the continuous phase is important and in other more than one property is required (e.g. concentration and temperature). Hence, for a general case, the relevant properties of the continuous phase is written in the form of a vector which is called the "continuous phase vector". The continuous phase vector is denoted by the symbol  $\mathbf{y}$

#### 2.1.2 Representation of a population of particles

Modeling is quantitative understanding of the system. Hence like we precisely described a single particle, we must describe a set of particles precisely. How can we do that? There are at least three ways:

1. Tag each and individual particles and give them some unique identification number (like each student has a roll number) and then make

a table for the internal and external coordinates. It is a very detailed description and possible only for a small population. Our institute does it regularly and many government organization including our Govt of India does it for a fairly large population of 120 crores (approx.  $10^{10}$  particles!) for giving ADHAAR card. For chemical engineering system, such a description can be used either when the system is small or a small portion of the system represents the large system accurately.

2. For chemical engineering systems, characterization of a population of particles required for large systems. For example, a crystallizer contains  $10^{13}$  particles per cubic centimeter. Also characterization is required on daily or hourly basis. Hence, a coarser approach is taken. Instead of measuring the internal coordinate of each particle, **the number (or mass) of particles in a given range of internal variable is measured.** Usually, a fixed amount of sample is taken (for example, unit volume of slurry from a crystallizer, or one kg of powder from the grinding product) and the number (or mass) of particles in a range of internal coordinate is measured. A familiar example is sieving. If we have spherical glass beads of a variety of size, we can select a series of sieves over a range of sizes and process 1kg of powder in the sieve. We then plot the mass fraction of particles in the range vs. the mean size in the upper and lower sieve size.

If the external coordinates are important, the discrete distribution will be in a multi-dimensional space where the mass/number of particles to be counted at a given space bin first and then they must be divided into size bins.

However, this represents the population of particles through a discrete function. While such representations of a population of particles are in great use in modeling and experiments, **the accuracy of this description will depend on the width of the size range.** Smaller the range, more accurate is the description. However, much accuracy could not be gained using this method because as the width of the range narrows down, the mass on each sieve reduces to very small amount giving statistical fluctuations.

3. In the limit where the width of the range shrinks to zero, the 'number' of particles in that range also shrinks to zero. This is a familiar problem. This is because we are trying to define an 'extensive property'

as point function. The mass/number of particles in a size and space range increase as the width of the range increases. This is like trying to define mass at a certain point. In microscopic mass balance equation mass is represented by density, which is the mass per unit volume, if the volume is sufficiently small.

Hence, we can define an intensive variable instead of 'The number of particles in a range'. First, we could define a quantity which is the number of particles in certain range of sizes per unit volume of crystallizer. But still, the number of particles per unit volume is extensive in the size variable. The 'number of particle per unit volume of crystallizer' will shrink and expand with the width of that range. Hence, to make it completely intensive, we should define 'number density' of particles as 'The number of particles in a given space and size range divided by the volume of the space and the width of the size range'. As the bin size shrinks, the number density converges to a definite value.

Hence, if  $N_x$  is the number of particles obtained in a certain size range from  $x$  to  $x + \Delta x$  collected from a volume  $\Delta V$  from a crystallizer, the number density will be defined as:

$$f_1(x, t) = \frac{N_x}{\Delta x \Delta V}$$

In the above definition  $f_1(x, t)$  converges to a certain value as  $\Delta x$  and  $\Delta V$  approaches the limiting value of 0. In the above illustration, the number density function is defined only in terms of one internal coordinate, i.e. size. However, in a general case, it can be defined over all internal and external coordinates. Hence, the general relation between number and number density is:

$$N = f_1(\mathbf{x}, \mathbf{r}) dV_{\mathbf{x}} dV_{\mathbf{r}}$$

## 2.2 A Batch Cooling Crystallizer

### 2.2.1 Understanding the problem

Once we describe a set of particles effectively by any one of these three methods, we are ready to proceed with the model. Let us now consider a batch cooling crystallizer. In this crystallizer, saturated solution of CS (conc.

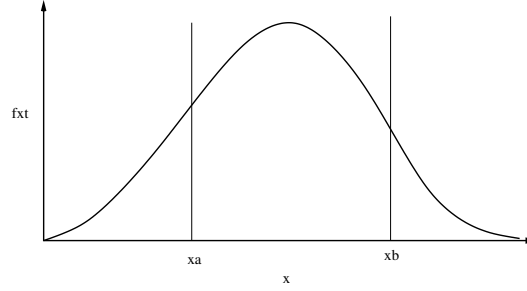


Figure 2.1: Deriving the growth equations

1.5 M) is cooled to 0 °C upon which it precipitates. Seed is supplied to the crystallizer so that nucleation does not happen to any appreciable extent. The particles grow larger by growth. The question that our "Manager" asking at this point is how the particle size distribution is changing with time.

The main phenomenon that is happening in the system is the growth of particles. So, **we must know the rate of growth of an individual particle** under a specified supersaturation. If the diameter of the particle is  $x$ , the growth rate of the particle is given by:

$$G(x, c(t)) = \frac{dx}{dt} = \frac{4D}{\rho_c} \left( \frac{1}{x} - \frac{1}{2\delta} \right) (c - c^*)$$

Hence, each of the particle in the crystallizer will grow according to this growth law and consume the supersaturation.

It can also be assumed that the system is well mixed and hence external coordinates are not important. Particles are also close to spherical and hence only one internal coordinate (particle radius) is important for describing the particles. Hence, the number density function can be written as:  $f_1(x, t)$ . Now, we must write a balance equation for the quantity of interest i.e.  $x + \Delta x$ . Because the quantity of interest is number density, we must write a number balance equation.

### 2.2.2 Population balance equation for pure growth

The balance equation for number density is called the 'population balance equation'. Let us write a number balance for the particles in the range  $[a, b]$ .

Where  $a$  and  $b$  are arbitrary. According to our discussion on number density function, the total number of particles per unit volume of crystallizer in this size range is given by  $\int_a^b f_1(x, t)dx$  and hence the rate of change of number of particles in this range is:

$$\frac{d}{dt} \int_a^b f_1(x, t)dx$$

The number of particles in this region changes due to growth. The particles immediately left of this boundary  $a$  will grow and will qualify to be considered within the range  $[a, b]$  and the particles which are just left of the boundary at  $b$  will leave this range and thereby reduce the number of particles in this range. Hence:

$$\frac{d}{dt} \int_a^b f_1(x, t)dx = \dot{N}_L - \dot{N}_R$$

where  $\dot{N}_L$  and  $\dot{N}_R$  are number of particles that enter and leave through left and right boundary respectively per unit time. Now consider a differential time interval  $dt$ . How many particles will enter the region of interest during this time interval? It will surely depend on the growth rate. If the growth rate is  $G(x, c(t))$ , particles will grow by a size  $G(x, c(t))dt$  during this interval and hence, the particles that are away from the boundary  $a$  by at most a size  $G(x, c(t))dt$  will be able to enter the region of interest. How many particles are there in that size range? It must be lower than size  $a$  and lies in a thin strip of thickness  $G(x, c(t))dt$ . As per the definition of number density, the number of particles in this small strip is  $f_1(x, t)G(x, c(t))dt$  evaluated at boundary  $a$ . Similarly, the number of particles that are leaving the boundary  $b$  is  $f_1(x, t)G(x, c(t))dt$  evaluated at the boundary  $b$ . Hence, the number balance can be written as:

$$\frac{d}{dt} \int_a^b f_1(x, t)dx = G(a)f_1(a, t) - G(b)f_1(b, t) \quad (2.1)$$

which can be written as:

$$\int_a^b \left[ \frac{\partial f_1(x, t)}{\partial t} + \frac{\partial}{\partial x} G(x) f_1(x, t) \right] dx \quad (2.2)$$

Because the interval  $[a, b]$  is arbitrary, the above equation can be written as:



$$\frac{\partial f_1(x, t)}{\partial t} + \frac{\partial}{\partial x} G(x) f_1(x, t) = 0 \quad (2.3)$$

This is the number balance equation for pure growth process. The model is not complete yet. We have to provide initial and boundary condition to this equation. The initial condition is the number density distribution of the seed. There can be various form of boundary conditions to this equation depending on the situation. For the current situation it can be written as  $f_1(0, t) = 0$ . Now the population balance equation is complete but it cannot be solved yet because it has two unknowns: one is the number density and the other is the  $c(t)$ . Hence we need another equation for  $c(t)$  which is obtained from mass balance.

### 2.2.3 Coupling the PBE with mass balance

Because the system is a batch, the total mass of CS remains constant. Initially it is mostly in form of dissolved CS and a little amount as seed. At later times, the amount as particle increases and the dissolved amount decreases. Hence, the mass balance can be written as:

$$c_0 V_0 + V_c(0) \rho = c(t)(V_0 - V_c) + V_c(t) \rho$$

where

$$V_c(t) = \int_0^\infty \frac{\pi}{6} x^3 f_1(x, t) dx$$

In writing the mass balance it is assumed that the total slurry volume remains constant.

### 2.2.4 Nucleation

So far we have modeled our crystallizer considering that we supply seed to the crystallizer. But in many instances, this is not the case. For many crystallizers, the seed crystals are nucleated inside the crystallizer.

Now, how does our population balance equation changes if we have nucleation? First, we note that the nuclei are very small particle close to zero size and can be thought of as a particle whose size is zero for practical purposes. Hence, nucleation happens at an 'boundary' of the PSD. This indicates that the natural way to incorporate nucleation event is through a boundary condition. The zero size particles produced by nucleation enters the particle size

distribution through the left boundary at  $x = 0$  and as we discussed before, the rate at which it enters the distribution is a product of its growth rate times number density at that size. Hence,

$$G(0, t)f_1(0, t) = \dot{N}$$

where  $\dot{N}$  is the nucleation rate. The nucleation rate is again a function of concentration and if homogeneous nucleation theory applies, it is given by:

$$\dot{N} = k_1 \exp\left[\frac{k_2}{-(\ln c(t)/c^*)^2}\right]$$

## 2.3 Number balance for open system

The balance equation that was written in terms of a large strip in particle internal coordinate axis, can also be written for a differential strip. This will obviate the need for the integration and the equation becomes:

$$\frac{d}{dt}f_1(x, t)dxV_c = G(x)f_1(x, t)V_c - G(x + dx)f_1(x + dx, t)V_c \quad (2.4)$$

Now, we can write a more general PBE considering inflow and outflow terms. If the particles entering with a number density  $f_{1,in}$  and the volumetric flow rate is  $\dot{V}_{in}$ , the number of particles that are entering in the size range is:  $f_{1,in}(x)dx\dot{V}_{in}$  and those leaving the reactor with the leaving  $f_1(x, t)dx\dot{V}_{out}$

Considering these streams, the number balance becomes:

$$\begin{aligned} \frac{d}{dt}f_1(x, t)dxV_c &= G(x)f_1(x, t)V_c - G(x + dx)f_1(x + dx, t)V_c \\ &\quad + f_{1,in}(x)dx\dot{V}_{in} - f_1(x, t)dx\dot{V}_{out} \end{aligned} \quad (2.5)$$

Which becomes:

$$\frac{d}{dt}f_1(x, t)V_c = -\frac{d}{dx}G(x)f_1(x, t)V_c + f_{1,in}(x)\dot{V}_{in} - f_1(x, t)\dot{V}_{out} \quad (2.6)$$

The above equation can be reduced for a steady operation of a MSMPR crystallizer, where no seed is supplied and nucleation is happening inside the crystallizer. Nucleation is treated as boundary condition as discussed before. Hence, for this case, the above equation becomes (for constant growth rate):

$$\frac{d}{dx}f_1(x) = -\frac{1}{G\tau}f_1(x) \quad (2.7)$$

The solution of this equation is:

$$f_1(x) = f_1(0)\exp\left(-\frac{x}{G\tau}\right) \quad (2.8)$$

$f_1(0)$  can be written in terms of the rate of nucleation as,

$$\dot{N} = Gf_1(0). \quad (2.9)$$

## 2.4 Exercise

**Exercise 2.1.** *Explain how will you describe a particulate system mathematically.*

**Exercise 2.2.** *Number density function is most often used in modeling of particulate systems. However there are cases where number is used instead of number density. Explain under which circumstances you will use number density and in which case you will use number and why.*

**Exercise 2.3.** *Write down the number balance equation for MSMPR crystallizer operating at steady state without any seed. Solve the equation for constant growth rate to get the steady state number density function. Show that the total mass of crystals per unit volume of slurry (usually termed as magma density,  $M_T$ ) for this case can be written as a function of operating parameters and physical constants. Develop the required mass balance equation for this case and draw the information flow diagram.*

**Exercise 2.4.** *Obtain the cumulative mass undersize distribution from the number density function. Can you obtain mass density function for this crystallizer?*

**Exercise 2.5.** *Consider the growth of very small perfectly spherical drops. The growth rate is not known. If we consider a pair of particles whose diameter are  $d_1$  and  $d_2$  respectively and at a certain instant  $d_1 > d_2$ , is it possible that at a later time  $d_1 < d_2$ ? Prove your answer.*

**Exercise 2.6.** Often the width of the particle size distribution (PSD) is a key property that needs to be controlled in operation of a crystallizer. The width is quantified by the ratio of the standard deviation and the mean of the PSD, which is known as Coefficient of Variance, (COV). Consider a seeded batch cooling crystallizer. Comment on the evolution of the COV for the following growth rates: (i)  $G(r) = \frac{k}{r}$  (ii)  $G(r) = k$  (iii)  $G(r) = kr^2$  where  $r$  is the particle radius and  $k$  is a constant incorporating factors other than particle size.

**Exercise 2.7.** Write down the number balance equation for MSMPR crystallizer operating at steady state without any seed. Solve the equation for constant growth rate to get the steady state number density function. Calculate the total mass of crystal per unit volume of slurry (usually termed as magma density,  $M_T$ ) for this case.

**Exercise 2.8.** How will you obtain the cumulative mass undersize distribution from the number density function? Can you obtain mass density function for this crystallizer?

**Exercise 2.9.** For MSMPR crystallizer, measuring the mass cumulative undersize, i.e. total mass of particles up to a size  $l$  (denoted by  $M(l)$ ) is an important quantity. For the case of MSMPR crystallizer show that:

$$\frac{M(x)}{M_t} = 1 - \left(1 + x + \frac{x^2}{2} + \frac{x^3}{3}\right)e^{-x} \quad (2.10)$$

where  $x = \frac{l}{G\tau}$  Hint: First obtain the equation for  $M(x)$  and then transform it in terms of  $M(x)$ .

**Exercise 2.10.** The mass density (similar to number density: just instead of counting the number, we measure the mass) can now be obtained using the usual procedure. Show that the mass density function for the MSMPR crystallizer is:

$$m(x) = \frac{x^3}{6}e^{-x} \quad (2.11)$$

**Exercise 2.11.** The mode of the distribution  $m(x)$  (i.e. where the distribution shows its peak) is an important quality control parameter. As a process control engineer, suggest a strategy to control this parameter. Your answer must be supported by clear mathematical deduction(s).

**Exercise 2.12.** 1. Obtain the number balance equation for MSMPR crystallizer operating at steady state with supplied seed. Consider a dilute system and neglect breakage/ aggregation of particles.

2. Write down the mass balance equation to complete the model. Show the information flow diagram. Modify your model to consider the effect of particle breakage.

**Exercise 2.13.** The number density function for a crystallizer is given by:

$$f_1(x) = f_0 \exp^{-\frac{x}{G\tau}} \quad (2.12)$$

where  $x$  is particle diameter. Obtain the expression for cumulative mass undersize in terms of dimensionless size parameter  $\frac{x}{G\tau}$ . Evaluate the median size by setting  $\frac{M(x)}{M_T} = 0.5$  and suggest an easy way to change median size.

**Exercise 2.14.** What is the relation between number and number density?

**Exercise 2.15.** What is the difference between internal and external coordinates?

**Exercise 2.16.** Explain how will you describe a particulate system mathematically.

**Exercise 2.17.** Relate the number density function to physically measurable quantities for i) well mixed vessel ii) vessel with spatial variation.

**Exercise 2.18.** Write down the population balance equation for pure growth process including inflow and outflow term. Simplify and solve this equation for number density for the case of constant growth rate and steady state operation of a MSMPR crystallizer. Explain how nucleation and growth rate can be deduced from the experimentally measured number density. How can such number density be measured?

**Exercise 2.19.** Consider any growth rate. If a particle is of size  $11 > 12$ , is it possible at some other time  $t > 0$   $12 > 11$ ? Give reason.

**Exercise 2.20.** Write the Population balance equation for growth of spherical particles from a super saturated solution. Clearly state the physical nature of the internal variable you used. Give at least two other internal variables that can be used. Write down the boundary condition for the equation. Mention some method that could be used to solve the equation.

**Exercise 2.21.** *If the nuclei are formed over a size range, modify the above model for that case. (10 min)*

**Exercise 2.22.** *Show that for a MSMPR crystallizer, the modal size is given by: In operation of MSMPR crystallizer, suddenly, the inlet concentration becomes double. What will be the effect on the avg particle size? Explain through model. (10min)*

**Exercise 2.23.** *We have a size distribution. How the SD of the distribution change for the three kinds of growth ?*

**Exercise 2.24.** *What is the difference between internal and external coordinates?*



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## Chapter 3

### The process of breakage

In the previous chapter, we have seen how growth modifies the number density function and how we can write a number balance equation. In this chapter we shall look into how breakage and aggregation modifies the number density function and how we can incorporate them into our number balance equation, i.e. the population balance model.

There is a fundamental difference between the process of particle growth and the process of breakage or aggregation. During growth, a particle of size  $x$  always grows to a particle  $x + dx$  where  $dx$  is sufficiently small. In other words, the size of a particle grows in a continuous fashion. In terms of internal coordinate, a particle moves along its internal coordinate in a smooth continuous fashion. On the other hand, the internal coordinate of particles changes by a 'jump' if aggregation and breakage take place. For example, the moment a particle breaks into two equal halves, the internal coordinates of the daughter particles change from  $x$  to  $x/\sqrt[3]{2}$ . In fact, the original particle no longer exists and it gave birth to two particles with their internal coordinates  $x/2$ . Hence, as if the particle 'jumped' in the internal coordinate axis to give two particles of internal coordinates  $x/2$ . Similar phenomenon happens for aggregation process. If two particles of size  $x/\sqrt[3]{2}$  aggregate, it forms a particle of size  $x$ . Hence, the change in internal coordinate corresponding to this change happened in a jump from  $x/\sqrt[3]{2}$  to  $x$ . Let us first discuss how to incorporate breakage terms in our number balance equation. To do that we have to first understand the physics of the breakage process.

### 3.1 The physics of the breakage process

Breakage occurs in many systems. For example, in polymer degradation, breakage of polymer chain may happen through hydrodynamic forces, thermal forces, ultrasound etc. Solid mineral rocks break into fine micron size powder in a ball mill, cells divide in a cell culture etc. Breakage is a generic name for all such processes. Because model needs everything quantitatively, we need to specify a breakage process with precision. The three things that are necessary and sufficient to specify breakage process are:

- The **frequency of breakage,  $\Gamma(x)$**  : The fraction of particles in a differential range of size that break per unit time.
- The **average number of daughter particles formed due to breakage  $\nu(x)$** : The average number of particles formed from the breakup of a single particle. This average number can be a fraction. For example, in a single breakage event, there may be 2 or 3 particles. But if observed for a sufficiently large number of such events, it is seen that 50% of time 2 particles are formed. Hence, the average number of daughter particles for this case is **2.5**.
- The daughter size distribution  **$P(x|x')$** : The probability density function for production of particles of size  $x$  from the break-up of a particle of size  $x'$ . This function must be a **normalized** probability density function.

These functions can be specified when the process is well understood. Let us consider the degradation of polymers. Polymers can be degraded many ways. One interesting degradation route for polymers is through ultrasound. In this case, the polymer chains are caught in the shear field and pulled from both ends. Due to symmetric pulling force, the polymer molecules break exactly from the mid point. This kind of breakage is called **mid point chain scission**. The rate of this breakage is dependent on the force of pulling. The longer the chain, larger the pulling force. Hence the rate of breakage must increase with increase in the length of the polymer molecule. If the internal coordinate for polymers is its molecular weight ( $x$ ), length is proportional to this variable. Hence, we may write the breakage rate as:

$$\Gamma(x) = kx^\alpha$$

However, if the length is too small, the pull is not sufficient to break the C-C bond. Hence, below a certain value of  $x$ , the breakage rate is zero. This may be incorporated as:

$$\Gamma(x) = k(x - x_l)^\alpha$$

where  $x_l$  is the limiting molecular weight below which breakage is not possible.

Thermal degradation of polymers is different. In this case, the polymer molecule may break from anywhere in the chain. This is called random chain scission. Under certain condition, the polymer chain may also break from one end. This is like taking each bid away from a chain. This is called 'chain end scission'. Breakage of solid particles is another example of breakage process. in this case, the particles are subjected to compressive stress. Due to this compressive stress, the micro-cracks in the material propagates and leads to fracture of the particles. Another example of breakage process is the division of cells. Cells normally do not undergo division unless they reaches a certain age. After that age, they divide into two halves, division rate depend on cell mass, substrate concentration etc.

The specification of the breakage function needs careful experimentation. For example, if we want to specify  $\Gamma(x)$  for breakage of solid particles in a mill where they break by the force of compression, we need to study individual particles under identical environment. Usually it has been observed that the larger particles break more frequently whereas the breakage of very fine particles are negligible. This is so because larger particles contain more number of micro cracks per unit volume. Hence, the breakage can be modeled as:  $\Gamma(x) = kx^a$  where  $k$  and  $a$  are the two parameters of the model. These two parameters are estimated using a machine where individual particles of a known size are compressed and the breakage events are monitored. The number of particles produced due to breakage and the daughter distribution function can also be monitored by similar experiments. Sometimes, some of the breakage function can be derived logically. For example, for ultrasonic breakage of polymers, the daughters are of exactly of same size and the number of daughter particles from a breakage event is exactly 2.0. For a given system, once we know all the breakage functions, we can write the number balance for breakage process.

### 3.2 Number balance for breakage

To write the number balance for breakage we shall imagine that any other process like growth, aggregation or in-out streams are not present and write the balance in a similar way as we wrote previously. We start by writing the balance for the number of particles residing in an elementary strip. The change in number of particles in this strip is due to breakage. **If particles in this size range breaks, they become smaller (at least smaller by an amount so that they are no more in this elementary strip) and hence the rate of breakage of particles in this strip will equal to the loss term.** The function  $\Gamma(x)$  gives the 'fraction of particles' breaking per unit time. Hence the number of particle breaking per unit time is given by  $\Gamma(x)f(x, t)dx$  because  $f(x, t)dx$  is the total number of particles in the elementary strip. Is this strip also gaining some particles? Surely, some of the larger size particles that are breaking will fall in this size range. How many such particles will be entering (rather jumping into) this range per unit time?

Let us consider another elementary strip at an arbitrary size  $x'$ . The number of particles breaking per unit time of this strip is given by  $\Gamma(x')f(x', t)dx'$ . Now, from this breakage, how many particles are produced? This is given by the breakage function  $\nu(x')$ . Hence, the total number of particles produced per unit time from breakage of particles in the elementary strip of thickness  $dx'$  around  $x'$  is  $\nu(x')\Gamma(x')f(x', t)dx'$ . Now, the question is how many of these particles are within the size range from  $x$  to  $x + dx$ ? For this we require the 'probability density function' for the daughter particles. Because  $P(x|x')$  is a density function,  $P(x|x')dx$  is the probability (fraction) of daughter particles falling in the size range from  $x$  to  $x + dx$  upon breakage of particles of size  $x'$ . Hence, **the number of daughter particles that falls in the size range from  $x$  to  $x + dx$  upon breakage of particles of size  $x'$  is:**

$$\nu(x')P(x|x')dx\Gamma(x')f(x', t)dx'$$

Now,  $x'$  was chosen arbitrarily and any  $x'$  larger than  $x$  may produce (depending on  $P(x|x')$ ) particles in  $x$ . To account for that, we must sum all such terms which is nothing but integrating the above term with  $x'$  which will give the total gain of particles by the small strip around  $x$ :

$$\int_x^\infty \nu(x')P(x|x')dx\Gamma(x')f(x', t)dx'$$

Hence, the number balance becomes:

$$\frac{f_1(x, t)dx}{dt} = -\Gamma(x)f_1(x, t)dx + \int_x^\infty \nu(x')P(x|x')dx\Gamma(x')f(x', t)dx' \quad (3.1)$$

Which becomes:

$$\frac{\partial f_1(x, t)}{\partial t} = -\Gamma(x)f_1(x, t) + \int_x^\infty \nu(x')P(x|x')\Gamma(x')f(x', t)dx' \quad (3.2)$$

### 3.2.1 Required properties of the daughter distribution function

The daughter distribution function is a probability distribution. Hence, the first property it must obey is the normalization condition or:

$$\int_0^\infty p(x, x')dx = 1 \quad (3.3)$$

Another property of importance is that the size of the particle produced must be less than the mother particle:

$$p(x, x') = 0 \quad \text{If } x > x' \quad (3.4)$$

The third constraint is the mass balance. It says that the mass of the daughter times the probability must integrate to the mass of the mother particle. Which can be expressed as:

$$\rho \frac{\pi}{6} x'^3 = \int_0^{x'} \nu(x) \frac{\pi}{6} x'^3 \rho p(x, x')dx \quad (3.5)$$

Another additional constraint the breakage function must satisfy is for the binary breakage is the symmetry condition given by:

$$p(x, x') = p(x - x', x') \quad (3.6)$$

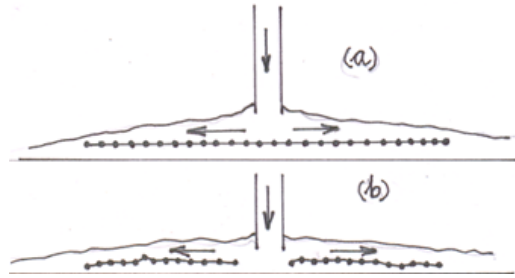
## 3.3 Discrete breakage equation

Sometimes a discrete equation is used for breakage:

$$\frac{dM_i(t)}{dt} = -k_i M_i(t) + \sum_i +1^N k_j M_j(t) B_{ij} \quad (3.7)$$

### 3.4 Exercise

**Exercise 3.1.** *Shear induced degradation of polymers is an important process. Polymer chains tend to break due to the shear field in the processing equipment and the molecular weight of the polymer decreases. This particular mode of degradation is very interesting because during this process the polymer molecule breaks approximately from the midpoint as shown in the figure below:*



The degradation reaction can be written as:

$$P(x) \rightarrow P(x/2)$$

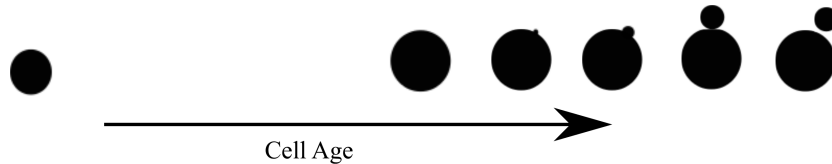
where  $P(x)$  represents the polymer species of molecular weight  $x$ . The rate constant for this degradation reaction is a function of molecular weight and other usual process conditions, e.g. temperature. The molecular weight dependence of the rate constant is given by:

$$k(x) = \kappa(x - x_1) \quad (3.8)$$

where  $\kappa$  is independent of molecular weight and  $x_1$  is the limiting molecular weight below which degradation does not occur.

1. Write down the population balance model for a batch process involving only shear-induced degradation of polymers.
2. Derive the equation for the  $i$ th moment of the PBE developed in part (a).
3. Discuss how the average molecular weight of the polymer can be expressed in terms of the moments and derive the equation describing the variation of average molecular weight with time.

**Exercise 3.2.** Cells of a particular bacterial species are growing and dividing as shown in the Figure below. Please note that the daughter cells can have a distribution of sizes. The cell culture grows in a batch fermentor



containing a nutrient and a product is formed inside the cells. Cell growth is dependent on cell mass and nutrient concentration. Formulate a population balance model to predict the transient cell mass distribution and nutrient concentration.

An improved version of this process is also used where a drug is added along with the nutrient. In absence of the drug, the product is stored inside the cells and is difficult to extract. The drug affects the cell membrane in such a way that the product is secreted outside the cells. Since this reduces the product concentration inside the cells, more amount of product is formed. But the drug also kills a portion of cells. The growth rate remains unaffected by the drug. Suggest possible modifications in the previous model so that it can be used for the improved process.

Forms of breakage and growth functions must be specified. Clearly justify the function chosen.

**Exercise 3.3.** • Write down the population balance equation for pure breakage process.

- What are breakage functions? Define and explain the breakage functions in brief.

**Exercise 3.4.** Write down the breakage functions for breakage of solid particles into two fragments or random size. The breakage rate is found to increase linearly with number of crystal defects present in a particle. Verify that the breakage functions satisfy all the required constraints.





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# Chapter 4

## Aggregation process

Aggregation is the process by which particles collide with each other and becomes indistinguishable. For example, if two drops of water collide, they become a single drop. Most of us have played with mercury coming out of a broken clinical thermometer. If two drops of mercury touch each other, they become a single larger drop. Aggregation of such drops may happen by aggregation of two or more than two drops. However, it can be shown that for dilute systems, binary aggregation is far more probable than ternary or higher order aggregation and in this chapter we shall only consider binary aggregation.

The binary aggregation depend on the formation of particle pairs. In modeling we have to define the number density of particle pairs. Previously, we defined number density of particles as a function of their internal and external coordinates. Similarly, we can define the number density of pair as:  $f_2(x, x', \mathbf{r}, \mathbf{r}', t)$ . We can measure this quantity in a similar way as we measured number density. For example  $f_2(x, x', \mathbf{r}, \mathbf{r}', t)dx, dx', d\mathbf{V}_\mathbf{r}, d\mathbf{V}_{\mathbf{r}'}$  is the total number of pairs in which one of the particle is from size  $x$  to  $x + dx$  and the other is from size  $x'$  to  $x' + dx'$  and the first particle is located in the elementary volume  $d\mathbf{V}_\mathbf{r}$  and second one is located at  $d\mathbf{V}_{\mathbf{r}'}$ . We shall later see that the number of pairs can be written in terms of number density of particles, i.e.  $f_1(x, \mathbf{r}, t)$

Now, we are interested in how many aggregation will happen over a time period of  $dt$  for the particles existing in the elementary strip  $dx$ . If the pair is made of particles far away so that they cannot come close enough within the period  $dt$ , they cannot form aggregate. Even in most cases, only a small fraction of particles that come to close proximity form aggregates.

Hence, *efficiency of aggregate formation* not only depend on the distance between particles in a pair, but also depend on the nature of particles, i.e their internal coordinates. It also depend on the external conditions like pH of the continuous phase. Such efficiency function is denoted by  $a(\mathbf{x}, \mathbf{x}', \mathbf{r}, \mathbf{r}', \mathbf{y}(\mathbf{t}))$ . Note that for aggregation to happen, the 'distance' between two particles need not to be zero. For example, when two spherical drop aggregates, their distance just need to be smaller than the sum of their radius.

Now let us consider the state of the newly formed particle after aggregation of two particles. The state of the final particles are given by a set of known functions. Let us denote these functions as

$$x = \zeta(\tilde{x}, x', )$$

where  $x$  is the internal coordinate of the newly formed particle. The external coordinate of the newly formed particle,  $\mathbf{r}$  can also be defined in a similar manner:

$$\mathbf{r} = \rho(\tilde{\mathbf{r}}, \mathbf{r}', )$$

. For example, if the particles are spherical liquid drops, the function  $\zeta$  is given by:

$$x = \sqrt[3]{\tilde{x}^3 + x'^3, )}$$

The second function can also be specified likewise. For example, the location of the newly drop may be specified as the center of the larger drop. i.e.

$$\begin{aligned} \mathbf{r} &= \tilde{\mathbf{r}} & \text{if } \tilde{x} > x' \\ &= \mathbf{r}' & \text{if } \tilde{x} \leq x' \end{aligned}$$

## 4.1 Number balance for aggregation

Again consider a small elementary strip in a single internal coordinate (e.g. particle diameter). The rate of change of number of particles in this strip is:

$$\frac{df_1(x, \mathbf{r}, t) dx d\mathbf{V}_{\mathbf{r}}}{dt}$$

which is due to aggregation alone. What happens due to aggregation? The particles in this small strip aggregate with other particles and hence they are no more eligible to be considered in this size interval (their size increases).

How many such losses happen per unit time? That depends on the number of possible pairs and the efficiency of aggregation. If we consider pairs which contribute to the aggregation in the small zone of interest, one of the particles must be in the state (or more precisely, in the vicinity of)  $x$  and  $\mathbf{r}$ . How many such pairs exists at a given time? This number is given by:  $f_2(x, x', \mathbf{r}, \mathbf{r}', t) dx, dx', d\mathbf{V}_{\mathbf{r}} d\mathbf{V}_{\mathbf{r}'}$  where  $x'$  and  $\mathbf{r}'$  are any internal and external coordinate respectively. The number of actual aggregation happening (i.e. the number of losses) per unit time is:

$$a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_2(x, x', \mathbf{r}, \mathbf{r}', t) dx, dx', d\mathbf{V}_{\mathbf{r}} d\mathbf{V}_{\mathbf{r}'}$$

. Because  $x'$  and  $\mathbf{r}'$  are arbitrary, the total loss term is found by integrating the above expression over the entire domain of  $x'$  and  $\mathbf{r}'$ :

$$\int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_2(x, x', \mathbf{r}, \mathbf{r}', t) dx, dx', d\mathbf{V}_{\mathbf{r}} d\mathbf{V}_{\mathbf{r}'}$$

Now, there will be **aggregation gain** as well. If we select any arbitrary state for one of the colliding particles, and want to know which particle should collide with these particles to form the particle in our elementary strip of interest, i.e. with internal and external coordinate  $x$  and  $\mathbf{r}$  respectively, the functions  $\zeta$  and  $\rho$  are to be used. We can simply plug in  $x', \mathbf{r}'$  and  $x, \mathbf{r}$  into these equation and obtain the required state of the other colliding particle as  $\tilde{x}$  and  $\tilde{\mathbf{r}}$ . Hence, the number of colliding pair in this case would be:

$$f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx', d\tilde{x}, d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\tilde{\mathbf{r}}}$$

But in the above calculation,  $f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t)$  and  $f_2(\tilde{x}, x', \tilde{\mathbf{r}}, \mathbf{r}', t)$  have been considered to be separate where actually they are not. Hence, **the same pair have been counted twice. To compensate for that a factor 1/2 is incorporated** in the gain term. The number of aggregate formed at  $x$  and  $\mathbf{r}$  therefore is:

$$\frac{1}{2} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx', d\tilde{x}, d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\tilde{\mathbf{r}}}$$

The total gain therefore will be the integration of the above term:

$$\frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx', d\tilde{x}, d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\tilde{\mathbf{r}}}$$

Hence, the balance equation is written as:

$$\begin{aligned} \frac{df_1(x, \mathbf{r}, t)dx d\mathbf{V}_{\mathbf{r}}}{dt} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx', d\tilde{x}, d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\tilde{\mathbf{r}}} \\ &- \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_2(x, x', \mathbf{r}, \mathbf{r}', t) dx, dx', d\mathbf{V}_{\mathbf{r}} d\mathbf{V}_{\mathbf{r}'} \end{aligned}$$

In the first integration term the differential is in terms of  $\tilde{x}$  and  $\tilde{\mathbf{r}}$  instead of  $x$  and  $\mathbf{r}$  and hence a **variable change from  $\tilde{x}$  to  $x$  and  $\tilde{\mathbf{r}}$  to  $\mathbf{r}$  in the integration is required**. This can be done as the functional relation between these variables are known through the functions  $\zeta$  and  $\rho$ . The formal process is to write the Jacobian of the transformation upon which the first integral term becomes:

$$\frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx', dx, d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\mathbf{r}} \left| \frac{\partial(\tilde{x}, \tilde{\mathbf{r}})}{\partial(x, \mathbf{r})} \right|$$

Now the like differential terms can be cancelled and the equation becomes:

$$\begin{aligned} \frac{\partial f_1(x, \mathbf{r}, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_2(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, t) dx' d\mathbf{V}_{\mathbf{r}'} \left| \frac{\partial(\tilde{x}, \tilde{\mathbf{r}})}{\partial(x, \mathbf{r})} \right| \\ &- \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_2(x, x', \mathbf{r}, \mathbf{r}', t) dx', d\mathbf{V}_{\mathbf{r}'} \end{aligned}$$

Now, for most cases, the pair density function can be written as:

$$f_2(x, x', \mathbf{r}, \mathbf{r}', t) = f_1(x, \mathbf{r}, t) f_1(x', \mathbf{r}', t)$$

with this substitution, the above equation becomes:

$$\begin{aligned} \frac{\partial f_1(x, \mathbf{r}, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_1(\tilde{x}, \tilde{\mathbf{r}}, t) f_1(x', \mathbf{r}', t) dx' d\mathbf{V}_{\mathbf{r}'} \left| \frac{\partial(\tilde{x}, \tilde{\mathbf{r}})}{\partial(x, \mathbf{r})} \right| \\ &- \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_1(x, \mathbf{r}, t) f_1(x', \mathbf{r}', t) dx', d\mathbf{V}_{\mathbf{r}'} \end{aligned}$$

Further, **if the system is well mixed**, the number densities are not a function of space variable. However aggregation efficiency inherently is a function of spacial location of the particles.

$$\begin{aligned} \frac{\partial f_1(x, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_1(\tilde{x}, t) f_1(x', t) dx' d\mathbf{V}_{\mathbf{r}'} \left| \frac{\partial(\tilde{x}, \tilde{\mathbf{r}})}{\partial(x, \mathbf{r})} \right| \\ &\quad - \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_1(x, t) f_1(x', t) dx' d\mathbf{V}_{\mathbf{r}'} \end{aligned}$$

Now, multiplying both sides of the above equation by  $d\mathbf{V}_{\mathbf{r}}$  and integrating wrt  $\mathbf{r}$  we have:

$$\begin{aligned} V(\Omega_{\mathbf{r}}) \frac{\partial f_1(x, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}'}} a(x', \tilde{x}, \mathbf{r}', \tilde{\mathbf{r}}, y(t)) f_1(\tilde{x}, t) f_1(x', t) dx' d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\mathbf{r}} \left| \frac{\partial(\tilde{x}, \tilde{\mathbf{r}})}{\partial(x, \mathbf{r})} \right| \\ &\quad - \int_{x'=0}^{x'=\infty} \int_{\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) f_1(x, t) f_1(x', t) dx' d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\mathbf{r}} \end{aligned}$$

Because the **external coordinates are not important**, the number density in the source term is written only in terms of  $\tilde{x}$  and hence only  $\frac{d\tilde{x}}{dx}$  term in the Jacobian exists. Now, defining:

$$a(x, x') = \frac{\int_{\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}'}} a(x, x', \mathbf{r}, \mathbf{r}', y(t)) d\mathbf{V}_{\mathbf{r}'} d\mathbf{V}_{\mathbf{r}}}{V(\Omega_{\mathbf{r}})}$$

the above equation becomes:

$$\begin{aligned} \frac{\partial f_1(x, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=\infty} a(\tilde{x}, x', y(t)) f_1(\tilde{x}, t) f_1(x', t) dx' \frac{d\tilde{x}}{dx} \\ &\quad - \int_{x'=0}^{x'=\infty} a(x, x', y(t)) f_1(x, t) f_1(x', t) dx' \end{aligned}$$

If the internal coordinate is volume, the function  $\zeta$  becomes:

$$x' + \tilde{x} = x$$

and hence the Jacobian is unity. It can also be assumed in many cases that the continuous phase has a **stable condition**. This equation then simplifies to:

$$\begin{aligned} \frac{\partial f_1(x, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=x} a(x - x', x') f_1(x - x', t) f_1(x', t) dx' \\ &\quad - \int_{x'=0}^{x'=\infty} a(x, x') f_1(x, t) f_1(x', t) dx' \end{aligned} \quad (4.1)$$



## 4.2 Estimation of aggregation frequency

Estimating the frequency and efficiency of aggregation is an involved task. For example, the case of gravity settling. Detailed models can be developed for the system and it can be shown that the aggregation frequency is given by:

$$a(x, x') = a_0(x'^{1/3} + x^{1/3})|x'^2 - x^2| \quad (4.2)$$

We can see that if the volumes of the particles are same, they settle at the same velocity and the probability of them to aggregate is zero.

For most collidal particles the force of gravity is negligible and they move in a brownian motion. In that case, the aggregation frequency is given by what is called a Brownian kernel. Which is given by:

$$a(x, x') = a_0(x'^{1/3} + x^{1/3})(x'^{-1/3} + x^{-1/3}) \quad (4.3)$$

To model collision efficiency, we need to understand the force acts between colloidal particles. Van dar waals attraction is the main attractive force between particles. Hence if only such forces are acting, every collision will be fruitful and the shelf life of a colloid will be at least four orders of magnitude lower than a second. Hence most colloids contain an electrical double layer which provide a repulsive force between particles.

## 4.3 Exercise

**Exercise 4.1.** *The kerosene-water system as described in question 3(a) maintains a steady state drop size distribution if the flow field inside the vessel is sufficiently turbulent. If the stirrer is stopped, aggregation is the only process to consider. Write down the PBE for this case considering drops to be perfect sphere. Will the PBE be different if you consider diameter of the drops as internal coordinate instead of volume? Explain.*

**Exercise 4.2.** *Imagine yourself as a R&D engineer in a food product manufacturing plant. Your plant produces a cereal called 'Granola Grin' which is sweetened granola nugget. Roasted granola come from a roasting unit which undergoes a process called granulation in the plant under your supervision.*

*The process is a batch process. First, the roasted granola (approximately 5mm in size) is fed to a rotating drum. Soon after feeding the roasted granola, a rotating bucket sprays a small amount of hot sugar syrup for the first 2*

minutes. The sugar syrup makes small aggregates of size 2 cm. The drum continues to rotate slowly at 15 rpm for a period of another 10 minutes. Then the rotational speed is reduced to 5 rpm and hot air is circulated through the drum for another 5 minutes. At the end, the product goes to the packaging section.

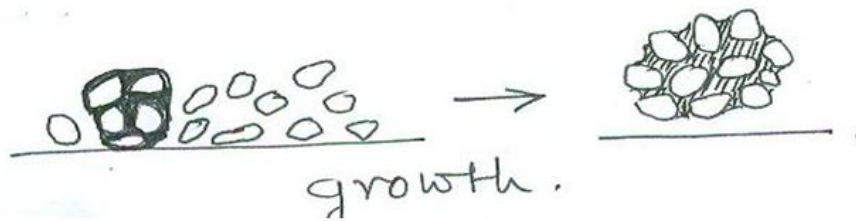
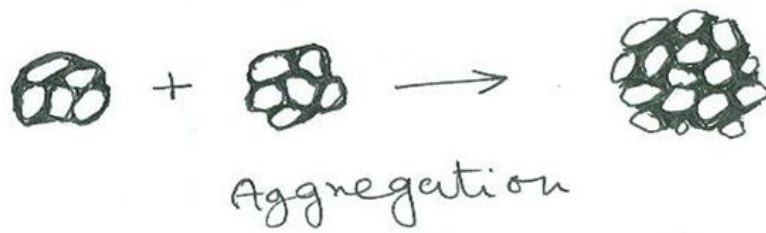
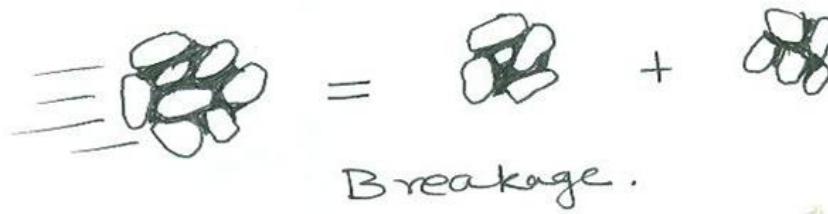
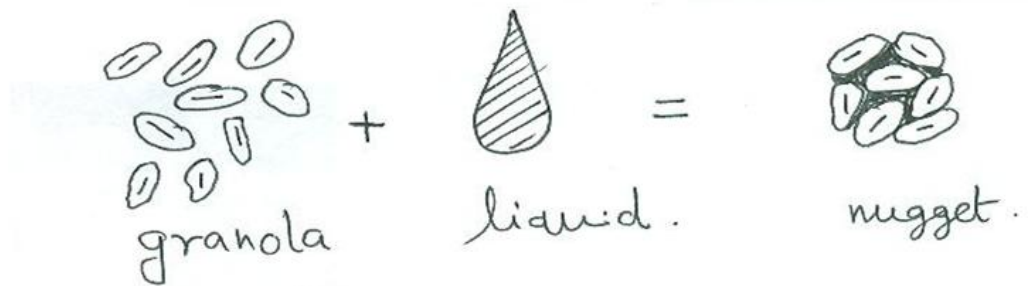
Despite the simple nature of this process, the manager noted that it is very difficult to get rid of 'dust' which is nothing but the single granola seed coated with sugar. Such 'dust' are difficult to recycle as they produce much sweeter product and because of this your company is losing market. They tried various things like changing the rotational speed, air flow rate etc, but could not form a systematic knowledge base. Finally they want to give modeling a try and asked you to formulate a population balance model for the process.

The shift in charge gave you the following details of the process: The granulation happens in the following steps: first is the nucleation of the lumps. As soon as we add the sugar syrup the lumps form. At the same time, the existing lumps start to gather mass around it and also some of the loose lumps break. Also sufficiently wet granules can coalesce with others. From my experience I've seen that the spray rate of the liquid and the rotating speed are very important. I can solve the problem if I'm allowed to spray more sugar syrup but the QC department does not allow it as it spoils the crispy nature of the nuggets.

1. What are the internal variables that are needed for representing the particles?
2. Are external coordinates important?
3. Which of the processes shown above should dominate in the system? Justify your answer.

Develop a population balance model for the above process. Make all necessary assumptions and justify them. State all assumptions clearly under a separate section named 'Model assumptions'. Suggest some way to minimize the fines on the basis of your model.

**Exercise 4.3.** Consider aggregation of perfectly spherical drops of liquid. Write down the aggregation population balance equation for (a) Internal coordinate is the surface area of particles. (b) Internal coordinate is the diameter of the particle. The aggregation kernel can be taken as constant.



**Exercise 4.4.** *Tiny drops of toluene containing a solute A are uniformly dispersed in water. Hexane drops of similar size containing a different non-reactive solute B are introduced into the system. Under the hydrodynamic condition inside the vessel, the drops continuously coalesce and break. What will be the concentration of A, B, hexane and toluene in an arbitrarily chosen drop after sufficiently long time? Will the relative rates of breakage and aggregation have any influence on the final concentration?*

**Exercise 4.5.** *In a particular ailment, pathogen cell colonies are produced inside a tissue. Cells grow (i.e. cell mass increases) and divide depending on the nutrition supply to the tissue. If a cell grows beyond a critical size, they migrate inside the tissue to make colonies containing 10 to 100 cells. Colonies containing less than 10 cells are rarely observed. While it is easier to destroy individual cells by using antibiotics, it is much more difficult to destroy a colony. Physicians want to know the factors (quantitatively) that affect the generation and maintenance of colonies. You have to help them by formulating a population balance model for the system. Follow these steps:*

1. *Write a brief one-page description of the system identifying key features. Use figures/schematics.*
2. *Identify the key particulate processes occurring in the system. Give reason for each process considered.*
3. *Define notation for each quantity; identify the internal coordinate(s) required for the system and mention if external coordinates are needed.*
4. *Write down the model equations along with required boundary conditions. Suggest a method to solve model equations.*

**Exercise 4.6.** *Reactive precipitation is a process where two chemicals A and B, soluble in the solvent S, react to give a sparingly soluble product C. The product nucleates and grows to produce matured particles. The small particles produced during nucleation, or early stage of growth may form aggregates. To prevent this, a stabilizer is usually added prior to the reaction. The stabilizer is adsorbed on the particle surface so that part of the surface is covered by stabilizer and becomes unavailable for growth. This coverage also prevents aggregation. However, the part of the surface that is covered by the stabilizer is also not available for growth. Hence, very small particles are formed in this kind of reactive precipitation. Model this system to predict the final PSD of the particles.*

**Exercise 4.7.** Consider a seeded batch cooling crystallizer. In this crystallizer, super-saturation is created by cooling the saturated solution to the desired temperature. Seed crystals of very small size are added to the crystallizer mature crystals. Uniform concentration is maintained by vigorous stirring. Unfortunately, stirring leads to breakage of crystals. However, very small crystals, which are smaller than 1 micron rapidly aggregate with other particles and excessive fine is not a problem. Formulate a population balance model for the abovementioned problem. The two main quantities of importance are the temporal particle size distribution and the concentration.

**Exercise 4.8.** Write down the aggregation population balance equation considering sphere equivalent diameter of particles as internal coordinate. Recast the equation in terms of particle volume as internal coordinate instead of diameter. Reduce it further for the case of constant aggregation kernel. Obtain the equation of zeroth moment for this PBE.

**Exercise 4.9.** Write down the aggregation PBE considering particle length as internal coordinates. (The Jacobian of the reansformation should be there)

**Exercise 4.10.** What is the unit of aggregation frequency?

**Exercise 4.11.** Two oil in water emulsions, both containing chemical A in the oil phase, are fed to a batch homogenizer. The concentration of A is different in the two emulsions. In the homogenizer intense shear induces both breakage and aggregation of drops. It is required to estimate the time that is required to form emulsion in which all drops are having the same concentration. Develop model equations for this case.

**Exercise 4.12.** In a controlled environment chamber as shown in Figure below, water vapor is formed at the lower part and is cooled at the upper part of the chamber to a temperature sufficiently below its dew point. Small drops condense on dust particles at the upper portion, which then grow both by further condensation and aggregation. Once a drop is larger than  $\sim 10$  micron, they start to fall.

1. If the above system is to be modeled using population balances, which internal co-ordinates will you use? What will be the continuous phase vector?
2. Write down the population balance equation for the above system.

3. *Comment on the form of (i) Breakage functions (ii) Aggregation frequency and (iii) Growth rates for the above system.*

**Exercise 4.13.** *Write down the population balance equation for pure aggregation problem. Solve the equation for constant aggregation frequency using Laplace transform method.*

**Exercise 4.14.** *Consider aggregation problem where droplets are forming like this. They never becomes a single sphere unless another joined. What are the internal coordinates?*



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## Chapter 5

# Solution of population balance equation

We have seen that the population balance equation is a complicated equation. For the growth process it is an partial differential equation, for breakage it is partial integro-differential equation and for aggregation it is a non-linear partial integro-differential equation. We have also seen that it is often coupled with many smaller models like growth rate of individual crystals, breakage rate and daughter distribution functions, aggregation frequency or mass balance involving continuous phase vector. They altogether form a very complicated set (almost certain to be non-linear) and numerical solution is inevitable. However, analytical solution of some simplified case can be obtained and such solutions are of great value in terms of benchmarking the numerical solution. In this chapter we shall first discuss about obtaining the moments of PBE and then a few analytical solution techniques will be discussed. Next a popular numerical solution technique for population balance equation will be discussed. It can be seen that even numerical solution is far from trivial. Often, new numerical techniques need to be invented in order to solve PBE efficiently.

## 5.1 Operations involving moments of the PBE

Let us examine how the moments of the breakage equation can be obtained. The breakage PBE is:

$$\frac{\partial f_1(x, t)}{\partial t} = -\Gamma(x)f_1(x, t) + \int_x^\infty \Gamma(x')f_1(x', t)\nu(x')P(x|x')dx'$$

Let us consider linear binary breakage (i.e.  $\nu(x) = 2.0$ ,  $\Gamma(x) = kx$ ) and random chain scission (i.e.  $P(x|x') = 1/x'$ ). Now, integrating the equation:

$$\begin{aligned}\frac{d\mu_0(t)}{dt} &= - \int_0^\infty kx f_1(x, t) + 2 \int_0^\infty \int_x^\infty kx' f_1(x', t) \frac{1}{x'} dx dx' \\ \frac{1}{k} \frac{d\mu_0(t)}{dt} &= -\mu_1(t) + 2 \int_0^\infty dx \int_x^\infty dx' f_1(x', t)\end{aligned}$$

The density is in  $x'$  but the limit for this variable is in a finite domain. To convert this into moments, this limit should be from 0 to  $\infty$ . This change usually possible after we change the limit as shown schematically below:

$$\begin{aligned}\frac{1}{k} \frac{d\mu_0(t)}{dt} &= -\mu_1(t) + 2 \int_0^\infty dx' \int_0^{x'} dx f_1(x', t) \\ \frac{1}{k} \frac{d\mu_0(t)}{dt} &= -\mu_1(t) + 2 \int_0^\infty x' f_1(x', t) dx' \\ \frac{1}{k} \frac{d\mu_0(t)}{dt} &= -\mu_1(t) + 2\mu_1(t) \\ \frac{1}{k} \frac{d\mu_0(t)}{dt} &= \mu_1(t)\end{aligned}$$

It can be seen that the equation for zeroth moment is dependent on first moment. This is usually the case and if the first moment depend on second moment and so on, the system can never be solved. This is called closure problem. Fortunately, for this case,  $\mu_1(t)$  is mass as must be a constant. Hence the evolution of the zeroth moment (which is the total number in this case) can be found. The zeroth moment varies linearly with time.

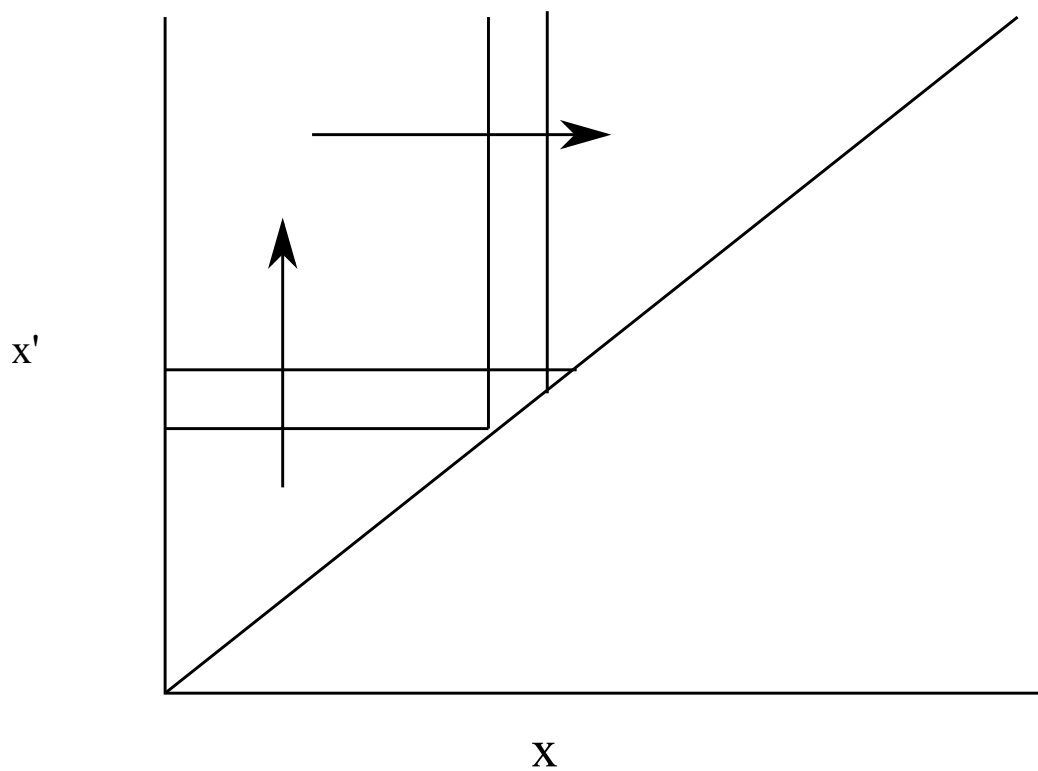


Figure 5.1: Schematic showing change of limit

## 5.2 analytical solution of PBE

Analytical solution of PBE involving breakage, growth and aggregation terms is not known to the author. However, analytical solution is possible for growth, breakage and aggregation equations when they are separated. Different methods are used for different equations. For example, pure growth equation may be solved using method of characteristics. On the other hand, aggregation equation may be solved using method of Laplace transform because of presence of convolution term. Breakage kernel often show similarity behavior and similarity solution is the popular method for analytical solution of breakage equation. We shall discuss these techniques in turn now.

### 5.2.1 Solution of growth equation: method of characteristics

Let us consider the solution of the growth equation:

$$\frac{\partial f_1}{\partial t} + \frac{\partial[-\alpha x^{\frac{2}{3}} f_1]}{\partial x} = 0$$

First let us reduce this equation to standard form:

$$a(x, t)f_x(x, t) + b(x, t)f_t(x, t) = c(x, t)$$

by substituting  $x^{\frac{2}{3}} f_1 = \hat{f}_1$ . With this substitution, this equation becomes:

$$x^{-\frac{2}{3}} \frac{\partial f_1}{\partial t} + (-\alpha) \frac{\partial f_1}{\partial x} = 0$$

The auxiliary equation for this pde is:

$$\frac{dt}{x^{-\frac{2}{3}}} = \frac{dx}{-\alpha} = \frac{d\hat{f}_1}{0}$$

From the first pair:

$$x^{\frac{1}{3}} + \frac{\alpha}{3}t = c$$

From the second pair:

$$\hat{f}_1 = \phi(c) = \phi\left(x^{\frac{1}{3}} + \frac{\alpha}{3}t\right)$$

transforming back:

$$f_1 = x^{-\frac{2}{3}}\phi(x^{\frac{1}{3}} + \frac{\alpha}{3}t)$$

Satisfying the initial condition:

$$f_{10}(x) = x^{-\frac{2}{3}}\phi(x^{\frac{1}{3}})$$

$$\phi(x^{\frac{1}{3}}) = x^{\frac{2}{3}}f_{10}(x)$$

$$\phi(\zeta) = \zeta^2 f_{10}(\zeta^3)$$

$$f_1 = x^{-\frac{2}{3}}(x^{\frac{1}{3}} + \frac{\alpha}{3}t)^2 f_{10}\{(x^{\frac{1}{3}} + \frac{\alpha}{3}t)^3\}$$

### 5.2.2 Solution of aggregation equation: method of Laplace transforms

Let us consider the aggregation equation with constant kernel:

$$\begin{aligned} \frac{\partial f_1(x, t)}{\partial t} &= \frac{1}{2} \int_{x'=0}^{x'=x} a_0 f_1(x - x', t) f_1(x', t) dx' \\ &\quad - \int_{x'=0}^{x'=\infty} a_0 f_1(x, t) f_1(x', t) dx' \end{aligned} \quad (5.1)$$

with the initial condition as:

$$f_1(x, 0) = N_0 g(x)$$

where  $N_0$  is the initial total number of particles and  $g(x)$  is a normalized distribution for particle size. The internal coordinate can be a non-dimensionalize number. Let us consider that the particle size is non-dimensionalize with the initial average mass. In this case, the average mass of particles at time  $t = 0$  will be 1.0. Hence:

$$\frac{\int_0^\infty x f_1(x, 0) dx}{\int_0^\infty f_1(x, 0) dx} = 1.0$$

Substituting  $f_1(x, 0) = N_0 g(x)$

$$\int_0^\infty x N_0 g(x) dx = \int_0^\infty N_0 g(x) dx$$

Since  $g(x)$  is a normalized function,

$$\int_0^\infty xg(x)dx = 1$$

Let us also introduce the following dimensionless quantities:

$$\tau = a_0 N_0 t$$

$$f(x, t)dx = \frac{1}{N_0} f_1(x, t)dx$$

$$\nu(\tau) = \int_0^\infty f(x, \tau)dx = \frac{N(t)}{N_0}$$

The PBE can be written as:

$$\begin{aligned} \frac{\partial f_1(x, t)}{\partial a_0 t} &= \frac{1}{2} \int_{x'=0}^{x'=x} f_1(x - x', t) f_1(x', t) dx' \\ &\quad - \int_{x'=0}^{x'=\infty} f_1(x, t) f_1(x', t) dx' \end{aligned} \quad (5.2)$$

Dividing both sides by  $N_0^2$

$$\begin{aligned} \frac{\partial f_1(x, t)/N_0}{\partial a_0 N_0 t} &= \frac{1}{2} \int_{x'=0}^{x'=x} \frac{f_1(x - x', t)}{N_0} \frac{f_1(x', t)}{N_0} dx' \\ &\quad - \int_{x'=0}^{x'=\infty} \frac{f_1(x, t)}{N_0} \frac{f_1(x', t)}{N_0} dx' \end{aligned} \quad (5.3)$$

The non-dimensional aggregation PBE now becomes:

$$\begin{aligned} \frac{\partial f(x, t)}{\partial \tau} &= \frac{1}{2} \int_{x'=0}^{x'=x} f(x - x', t) f(x', t) dx' \\ &\quad - \int_{x'=0}^{x'=\infty} f(x, t) f(x', t) dx' \end{aligned} \quad (5.4)$$

with the initial condition  $f(x, 0) = g(x)$ . The initial mass in the system is given by:

$$\int_0^\infty x f_1(x, 0) dx = \int_0^\infty x N_0 g(x) dx = N_0$$

Hence, the mass conservation becomes:

$$\int_0^\infty x f_1(x, \tau) dx = N_0$$

$$\int_0^\infty x f(x, \tau) dx = 1$$

Now, we take Laplace transform of this equation:

$$\begin{aligned} \frac{\partial \bar{f}(s, \tau)}{\partial \tau} &= \frac{1}{2} \int_0^\infty e^{-sx} dx \int_0^x f(x - x', \tau) f(x', \tau) dx' \\ &\quad - \int_0^\infty e^{-sx} dx f(x, \tau) \int_0^\infty f(x', \tau) dx' \end{aligned} \quad (5.5)$$

Changing limit of the first integral term:

$$\begin{aligned} \frac{\partial \bar{f}(s, \tau)}{\partial \tau} &= \frac{1}{2} \int_0^\infty dx' \int_{x=x'}^\infty dx e^{-sx} f(x - x', \tau) f(x', \tau) \\ &\quad - \int_0^\infty e^{-sx} dx f(x, \tau) \int_0^\infty f(x', \tau) dx' \end{aligned} \quad (5.6)$$

Substituting  $x - x' = u$ ,

$$\begin{aligned} \frac{\partial \bar{f}(s, \tau)}{\partial \tau} &= \frac{1}{2} \int_0^\infty e^{-sx'} f(x', \tau) dx' \int_0^\infty e^{-su} f(u, \tau) du \\ &\quad - \int_0^\infty e^{-sx} dx f(x, \tau) \int_0^\infty f(x', \tau) dx' \end{aligned} \quad (5.7)$$

$$\frac{\partial \bar{f}(s, \tau)}{\partial \tau} = \frac{1}{2} \bar{f}(x, \tau)^2 - \nu(\tau) \bar{f}(x, \tau) \quad (5.8)$$

The required initial condition for this equation can be found by taking the laplace transform of the initial condition:

$$\bar{f}(s, 0) = \bar{g}(s)$$

Because  $\nu(\tau)$  is the total number of particles, its evolution can be obtained from the moment equation and is given by:

$$\frac{d\nu(\tau)}{d\tau} = -\frac{1}{2}\nu(\tau)^2, \quad \nu(0) = 1$$



whose solution is:

$$\nu(\tau) = \frac{2}{2 + \tau}$$

Now, the nonlinear ODE can be transformed to linear ode by writing it in terms of  $\frac{1}{\bar{f}}$  which is:

$$\frac{\partial \frac{1}{\bar{f}(s, \tau)}}{\partial \tau} = -\frac{1}{2} + \nu(\tau) \frac{1}{\bar{f}(s, \tau)} \quad (5.9)$$

The solution is:

$$\bar{f}(s, \tau) = \left( \frac{2}{2 + \tau} \right)^2 \frac{\bar{g}(s)}{1 - \left( \frac{2}{2 + \tau} \right) \bar{g}(s)}$$

If the intital particle is monodispersed, with dimensionless size unity,  $\bar{g}(s) = e^{-s}$ . With this, the rhs can be expanded in series:

$$\bar{f}(s, \tau) = \frac{2}{2 + \tau} \sum_0^{\infty} \left( \frac{2}{2 + \tau} \right)^n e^{-s(n+1)}$$

This series can be inverted to:

$$f(x, \tau) = \frac{2}{2 + \tau} \sum_0^{\infty} \left( \frac{2}{2 + \tau} \right)^n \delta(x - n - 1)$$

### 5.2.3 Solution of breakage equations: similarity analysis

#### Similarity analysis of breakage equation

The breakage equation is:

$$\frac{\partial f_1(x, t)}{\partial t} = -\Gamma(x) f_1(x, t) + \int_x^{\infty} \Gamma(x') f_1(x', t) \nu(x') P(x|x') dx'$$

Integrating the above equation and defining:  $F(x, t) = \int_0^x f_1(x', t)$  we obtain:

$$\frac{\partial F(x, t)}{\partial t} = \int_x^{\infty} \Gamma(x') G(x|x') \frac{\partial F_1(x', t)}{\partial x'} dx'$$

where

$$G(x|x') = \frac{\nu(x')}{x'} \int_0^x d\zeta \zeta P(\zeta|x')$$

Now, assuming the self similar form  $F(x, t) = \phi(\eta)$  and  $\eta = x/h(t)$  (the form of  $h(t)$  is yet unknown) and similar breakage (i.e.  $G(x|x') = g(\frac{x}{x'})$  and power law breakage frequency ( $\Gamma(x) = Kx^\alpha$ ) the above equation becomes:

$$-\eta\phi'(\eta)\frac{h'(t)}{h(t)^{\alpha+1}} = K \int_{\eta}^{\infty} \eta'^{\alpha} g\left(\frac{\eta}{\eta'}\right) d\phi(\eta')$$

Now, the similarity solution will exist if the term  $\frac{h'(t)}{h(t)^{\alpha+1}}$  is a constant. The value of the constant can be chosen arbitrarily. Let us chose it to be  $-K$ . In this case, the similarity equation becomes:

$$\eta\phi'(\eta) = \int_{\eta}^{\infty} \eta'^{\alpha} g\left(\frac{\eta}{\eta'}\right) d\phi(\eta')$$

Which can be written as (for  $\alpha = 1$ )

$$\eta \frac{d\phi(\eta)}{d\eta} = \int_{\eta}^{\infty} \eta' g\left(\frac{\eta}{\eta'}\right) \frac{d\phi(\eta')}{d\eta'} d\eta'$$

Defining  $\psi(\eta) = \frac{d\phi(\eta)}{d\eta}$  the above equation becomes:

$$\psi(\eta) = \int_{\eta}^{\infty} \frac{\eta'}{\eta} g\left(\frac{\eta}{\eta'}\right) \psi(\eta') d\eta'$$

For uniform breakage  $P(x|x') = 1/x'$  and hence  $G(x|x') = (x/x')^2$  which means  $g(\eta/\eta') = (\eta/\eta')^2$ . Hence, for this type of breakage, the similarity equation becomes:

$$\psi(\eta) = \int_{\eta}^{\infty} \frac{\eta}{\eta'} \psi(\eta') d\eta'$$

Differentiating the above equation and applying Leibnitz rule: The form of the similarity equation is:

$$\psi'(\eta) = -\psi(\eta) + \int_{\eta}^{\infty} \frac{1}{\eta'} \psi(\eta') d\eta'$$

with  $\psi(0)$  as known initial condition( in terms of the similarity variable)  
Differentiating the above equation with respect to  $\eta$  (using Leibnit's rule)

$$\psi''(\eta) = -\psi'(\eta) - \frac{1}{\eta} \psi(\eta)$$

Rearranging:

$$\eta\psi''(\eta) + \eta\psi'(\eta) + \psi(\eta) = 0$$

Taking laplace transform: (Formulae taken from pp277 Kreyszig)

$$-2s\bar{\psi} - s^2 \frac{d\bar{\psi}}{ds} + \psi(0) - \bar{\psi} - s \frac{d\bar{\psi}}{ds} + \bar{\psi} = 0$$

Rearranging:

$$-s(s+1) \frac{d\bar{\psi}}{ds} - 2s\bar{\psi} = -\psi(0)$$

Rearranging:

$$\frac{d\bar{\psi}}{ds} + \frac{2}{s+1} \bar{\psi} = \frac{\psi(0)}{s(s+1)}$$

The integrating factor for this linear equation is  $(s+1)^2$  and the solution (taking the constant of integration as 0) is:

$$\bar{\psi}(s) = \psi(0) \left[ \frac{s}{(s+1)^2} + \frac{\ln(s)}{(s+1)^2} \right]$$

This can be inverted to obtain the solution.

## 5.3 Numerical Solution of population balance equation

A large number of numerical techniques are available to solve the population balance equation. Finite difference, finite volume, finite elements are among the popular ones. But there is one discretization method that is very popular and versatile. This is known as fixed pivot technique. We shall discuss this technique.

### 5.3.1 discretization of the breakage equation

The PBE is a partial integro-differential equation. Numerical methods like finite difference is seldom used. This equation is often solved by finite volume discretization. In most of the cases of practical importance the particle size spans over many orders of magnitude. For example, if we consider aerosol dynamics, we have small particles of nanometer size as well as centimeter

### 5.3. NUMERICAL SOLUTION OF POPULATION BALANCE EQUATION 57

size particles. So, it spans seven orders of magnitude. Hence a linear grid capable of capturing the small size particles will have  $10^7$  grid points which signify  $10^7$  differential equations.

Hence we generally use what is called a geometric grid. We start with a node located at a very small value of size axis, say 1nm, then every successive node point is multiplied by a ratio, (say 2) to obtain the next node. Hence, the  $n$ th node will be located at  $2^n$  on the size axis. Therefore, to cover up up-to  $10^7$  nm in size axis, we need only 23 node points and hence only 23 ODE's are to be solve. It can also be noted that although the grid is very coarse at large size, fine grid (at least up to 1nm) is not needed to characterize larger particles. In practical cases we can solve several hundred ode without trouble and hence the geometric ratio is much less than 2. However, the grid generated is a coarse grid and the accuracy of the algorithm must be monitored.

Let us consider the breakage equation:

$$\frac{\partial f_1(v, t)}{\partial t} = -\Gamma(v)f_1(v, t) + \int_v^\infty \Gamma(v')f_1(v', t)\nu(v')P(v|v')dv'$$

Integrate over the  $i$ th bin: and denoting  $N_i = \int_{v_i}^{v_{i+1}} f_1(v, t)dv$  we get:

$$\frac{dN_i}{dt} = - \int_{v_i}^{v_{i+1}} \Gamma(v)f_1(v, t)dv + \int_{v_i}^{v_{i+1}} \int_v^\infty \Gamma(v')f_1(v', t)\nu(v')P(v|v')dv'dv$$

Now, in this discretization, technique, the number density is approximated as:

$$f_1(v, t) = \sum N_i \delta(x - x_i)$$

substituting this in the rhs of the above equation and using the property of Dirac-delta function, the first term becomes  $\Gamma_i N_i$ . The second term needs some manipulation:

First we note that the particles formed by breakage may not form on the pivots. Hence, non pivot particles must be assigned to the pivots. During this assignment, the mass and number of particles must be preserved. If  $n(v)$  particles are formed at size  $v$  which is between  $i^{\text{th}}$  and  $(i+1)^{\text{th}}$  pivots,  $L(v)$  particles must be assigned to the  $i^{\text{th}}$  pivot and  $R(v)$  particles must be assigned to the  $(i+1)^{\text{th}}$  pivot so that:

$$L(v) + R(v) = n(v)$$

$$x_i L(v) + x_{i+1} R(v) = v n(v)$$

Solving these equations:

$$R/n = r_{i,i+1}(v) = (v - x_i)/(x_{i+1} - x_i)$$

$$L/n = l_{i,i+1}(v) = (x_{i+1} - v)/(x_{i+1} - x_i)$$

Hence, the birth term for  $i^{\text{th}}$  pivot will have contribution from the left (with the right fraction) and from the right (with the left fraction) 'inter pivot' regions. Hence the total birth term can be re-written as:

$$\int_{x_{i-1}}^{x_i} \int_v^{\infty} r_{i-1,i}(v) \Gamma(v') f_1(v', t) \nu(v') P(v|v') dv' dv + \int_{x_i}^{x_{i+1}} \int_v^{\infty} l_{i,i+1}(v) \Gamma(v') f_1(v', t) \nu(v') P(v|v') dv' dv$$

Now, substituting the approximate expression for number density and considering binary breakage:

$$\begin{aligned} & 2 \sum_{x_k \geq x_i} N_k \int_{x_{i-1}}^{x_i} r_{i-1,i}(v) \Gamma_k P_k(v) dv + 2 \sum_{x_k \geq x_i} N_k \int_{x_i}^{x_{i+1}} l_{i,i+1}(v) \Gamma_k P_k(v) dv \\ & 2 \sum_{x_k \geq x_i} \Gamma_k N_k \left( \int_{x_{i-1}}^{x_i} r_{i-1,i}(v) P_k(v) dv + \int_{x_i}^{x_{i+1}} l_{i,i+1}(v) P_k(v) dv \right) \end{aligned}$$

denoting the bracketed term as  $n_{ik}$ , the breakage equation becomes:

$$\frac{dN_i}{dt} = -\Gamma_i N_i + 2 \sum_{x_k \geq x_i} n_{ik} \Gamma_k N_k$$

for uniform breakage  $P_k = 1/x_k$  and  $n_{ik}$  becomes:

$$\frac{1}{2x_k} (x_{i-1} - 2x_i + x_{i+1})$$

Note that  $n_{ik}$  is known as soon as the grid (i.e. all  $x_i$ s) is defined. Now the 'partial integro-differential equation' is reduced to a set of ODE's which can be solved readily.

## 5.4 Exercise

**Exercise 5.1.** Write down the population balance equation for pure aggregation. Derive the equation for zeroth and first moments for constant aggregation kernel.

**Exercise 5.2.** What do you understand by 'closure problem' in context of moment equations?

**Exercise 5.3.** Write down the population balance equation considering nucleation, growth and breakage. Show that the equation for  $j$ th moment for constant growth rate ( $G$ ) and linear breakage rate ( $B=Box$ ) is:

$$\frac{d\mu_j}{dt} = G_j\mu_{j+1} + \frac{1-j}{1+j}B_0\mu_{j+1}$$

**Exercise 5.4.** What are breakage functions? Explain the breakage functions with example.

**Exercise 5.5.** Consider breakage of polymer molecules in a well-mixed vessel. If the particles undergo mid-point chain scission and the breakage is linear, specify all breakage functions. Breakage is not possible below a limiting molecular weight. Verify whether the breakage functions satisfy all required constraints. Derive the equation for  $j$ th moment for this case.

**Exercise 5.6.** Write down the breakage population balance equation and obtain the equation for zeroth, first and second moment for linear breakage rate and binary random break-up.

**Exercise 5.7.** Derive the moment of the growth equation.

**Exercise 5.8.** Write down the population balance equation for pure aggregation. Derive the equation for zeroth and first moments for constant aggregation kernel.

**Exercise 5.9.** What do you understand by 'closure problem' in context of moment equations?



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# Chapter 6

## Kinetic Monte Carlo Simulation

Monte Carlo is a generic name and we must define the goal of this chapter precisely. Monte Carlo is the name of a location in the city of Monaco which is famous for its casino. This has given rise to the practice in the scientific community to call numerical procedure that involves random numbers as 'Monte Carlo simulations'. There are a variety of computations that are called Monte Carlo Simulations. One example is use of random number in evaluating a multi-dimensional integral. We shall discuss that in brief later. Such integrals are often encountered in statistical mechanics and the aim is to evaluate equilibrium properties and time is not involved in such calculations. In our case we 'simulate' the evolution of particulate systems using random numbers. **Book keeping of time is an integral part of such simulations** and hence these simulation techniques are called Kinetic Monte Carlo simulation.

### 6.1 Random variables and Distribution Functions

First let us give some examples of random variables:

- The number of cosmic particles impinging on a definite area of the earth's surface a particular time interval is a random variable. This is because this quantity is dependent on a large number of random factors.

- The number of calls arriving at a call center from 10 am to 11 am.
- The deviation of a bullet from the center of the bull's eye.
- The instantaneous velocity of turbulence.

For a deterministic variable, if the circumstances are defined, the variable has a definite unique value. For example, if a particle is dropped from a particular height, its free fall velocity after a certain time is given by a single number and hence is a deterministic variable. In contrast, random variables can take a variety of values even for a well defined set of conditions. Therefore, in order to know a random variable, it is first and foremost necessary to know the values that it can assume. However, only a list of values is not sufficient to draw essential conclusions. We also need to know how often (i.e. the probability) it assumes a particular value. Hence, like a deterministic variable has a single value and specification of that value is sufficient, random variables are specified when all possible values are listed and their corresponding probabilities are listed.

Let  $\zeta$  be a random variable and  $x$  be an arbitrary real number. The probability that  $\zeta$  will take on a value less than  $x$  is called the distribution function of probabilities of the random variable  $\zeta$ :

$$F(x) = P\zeta < x$$

A random variable is a variable quantity whose values depend on chance and for which a distribution function of probabilities has been defined.

### 6.1.1 Examples of random variables and its distribution function

Let  $\mu$  be a random variable defined as “the number of heads in a sequence of 5 independent tossing of a fair coin”. Note that this is a discrete random variable. The values that  $\mu$  can take are 1, 2, 3, 4, 5 and no other value is possible. Now, to specify it completely, we have to specify the cumulative probability distribution function  $F(x)$ .

We know that

$$\binom{P_n(m) = \mathbf{P}\mu = m}{np^mq^{n-m}}$$

Hence the cumulative distribution function can be defined as:

## 6.2 Random numbers and Pseudo-random numbers

A random number is a random variable with equal probability of its occurrence in an interval, usually from 0 to 1.0. To get a set of random numbers, we may follow a truly random process and obtain a sequence of random values which can be considered as random numbers. But for practical usage, we want computers to generate random numbers. Hence we need an algorithm for generation of random numbers. Now, there is a fundamental fallacy in this statement. In principle if we have an algorithm for producing random numbers, that will no longer be a random number. Therefore, the random numbers produced by computers (like the Rnd# button in your calculator) are actually **pseudo random numbers**. For this set of lectures we shall pretend that pseudo random numbers are sufficient for our simulations.

## 6.3 Mean field versus stochastic model

So far we have modeled various systems using mass, momentum, energy and (in some cases) number balance equation. All **these equations quantify 'average' properties and is known as 'mean field model'**. In mean field model, the evolution of the system is governed by the mean 'rate' of a process, like rate of mass in, rate of consumption, rate of breakage etc. In reality, this rate is an average of various 'events' happening in or around the system.

For example, let us consider the process of particle breakage under unvarying system condition. If the mean number of breakage occurring for a particle of size  $x$  per unit time is 30%, it does not necessarily mean that for any given second exactly 30% number of particles of size  $x$  will break. In practice, sometimes 31% particles may break, sometime 29% breakage may happen. On an average, there will be 30 breakage.

It seems to be too much to ask for such minuscule details. However, there are many systems where such differences matter. One obvious example is small systems. **The mean field approximation is valid when there are a large number of entities** (particles, molecules) in the system of concern. For example, a crystallizer with volume 10L will have about  $10^{17}$  particles. But if crystallization is happening inside surfactant micelles, there will be 1-4 molecules in each micelles and at most two crystals in a micelle. Hence, averaging may not work for the later case. Usually the stochastic model

matches with the deterministic model as the number of entities (or the system size) is increased. However, some cases, even the large population limit of stochastic model does not match with the mean field model. Often non-linearity is the reason for such behavior and the only way forward for such cases is stochastic modeling.

Like rate of a process determines the evolution of a system in a mean field model, the occurrence of an 'event' is responsible for evolution of the system in stochastic simulations. In an event, an entity (molecule/atom for reaction, particles for particulate systems) changes its form. It may be noted that processes may be described by a combination of movement and alteration of states of entities. In a stochastic simulation events are administered on the system and the state of the system is tracked in time.

## 6.4 Kinetic Monte Carlo

There are basically two types of Kinetic Monte Carlo (KMC) simulations: one is "event driven" KMC and the other is "time driven" KMC. In this chapter we shall consider event driven KMC. Let us consider the process of particle breakage as an example and the case where average rate of breakage, average number of daughter particles and the daughter distribution function is known.

### 6.4.1 Selection of system size

In KMC, the evolution of a system (for example, a box containing 100 particles) is followed in time. Hence, the first step is to identify the system. The system simulated is often smaller in size from the true physical system due to computational limitations. Therefore, the system size is selected in such a way that it is large enough to represent the true system and yet small enough to complete the computation in reasonable time. Once the system size is decided, we must represent the system in terms of precise quantities. For example, we can represent a system containing  $n$  drops of a pure liquid by a vector  $A[t] = [v_1v_2v_3v_4]$ . In this case, the drops are spherical and of single component and hence, a single variable, the volume, can describe it properly. If the location of the drop is also to be considered, the array becomes:  $A[t] = [v_1v_2v_3v_4; r_1r_2r_3r_4]$

### 6.4.2 Interval of Quiescence (IQ)

The system is now defined. Now we have to allow the system to evolve in time by administration of events. To do so, we have to **find out the time gap between the events**. In the gap between events, the system remains quiet and this time span is termed as "Interval of Quiescence (IQ)". It is clear that the IQ is dependent on the rate of events. On an average, IQ becomes shorter if the rate of event is higher. But remember, since the system is stochastic, this applies only in an average sense. Individual values of IQ is completely random. Hence, **IQ is a random variable with a known probability distribution**. The mean value of this variable should match with the mean interval between events. Because the rate of events dependent on the state of the system,  $A(t)$ , IQ is also dependent on the state of the system.

Let us denote the random variable IQ by the symbol  $T$  and the clock time by the symbol  $t$ . If for a given instant (i.e. for a particular value of  $t = t^*$ ) the IQ is given by  $T^*$ , an event will occur (with probability=1) precisely at clock time  $t^* + T^*$ . Since  $T^*$  is dependent on the condition of the system at  $t = t^*$ , the probability distribution of the random variable  $T$  would have such dependance. This relation will be derived next.

Because  $T$  is a random variable, we cannot have a deterministic relation between system parameters (or breakage functions) and  $T$ . All we can specify about this random variable is its 'probability density distribution'. Let us define  $F_T(\tau|t)$  as:

$$F_T(\tau|t) = Pr\{T < \tau|A(t)\} = 1 - Pr(T \geq \tau|A(t)) = 1 - P_T$$

It can be seen that  $F_T(\tau|t)$  is a cumulative quantity of the probability density function and hence itself is a probability. Its meaning is also clear from the definition. The meaning of  $P_T$  is also clear which can be read as: **"probability that the event happens after elapse of time  $\tau$ "**. It follows:

$$P_T(\tau + d\tau|t) =$$

$$P_T(\tau|t) \times Pr[\text{None of the quiescence disturbing events happend from } \tau \text{ to } \tau + d\tau]$$

or,

$$P_T(\tau + d\tau|t) =$$

$$P_T(\tau|t) \times \{1 - Pr[\text{One of the quiescence disturbing events happend from } \tau \text{ to } \tau + d\tau]\}$$

Now, what is the probability that one of the quiescence disturbing events happened during the small time window  $d\tau$ ? If the system is observed for

a time period (say time  $\tau_e$ ) which is much larger than  $d\tau$  and the number of events are counted (say  $N_e$ ) during this period, the probability would be  $(N_e/\tau_e) \times d\tau$ . But,  $N_e/\tau_e$  is the rate of the process occurring (breakage in this case) in the system at time  $t + \tau$ . Hence,

$$P_T(\tau + d\tau|t) = P_T(\tau|t) \times \{1 - \Gamma[A(t + \tau)d\tau]\}$$

Which becomes:

$$\frac{dP_T}{d\tau} = -P_T\Gamma[A(t + \tau)]$$

It is clear from the derivation that  $\Gamma$  is the total rate of a process.

### 6.4.3 Sampling of a certain distribution

Now, we know the probability distribution (rather the cumulative probability distribution,  $P_T$  or  $F_T$ ) of the IQ. In simulation we would rather require a 'sample' from such a distribution in order to advance the system clock and administer the event. In other words, if we take a large number of such IQ samples, they should follow the distribution shown above. Please note that only one sample needs to be drawn in order to advance the system clock. Once the sample IQ is considered and the time is advanced, the distribution function for IQ changes according to the equation given. Hence the next sampling actually drawn from a different distribution.

**How the sampling is done?** The following method is used to generate random samples so that finally it follows a pre-specified distribution. First let us consider a discrete distribution of three events:  $E_1$ ,  $E_2$  and  $E_3$  with probability of occurrence 0.45, 0.45 and 0.1 respectively. The normalized cumulative plot of this distribution is shown in Fig. Since it is normalized, the Y-axis will always span from 0 to 1. Now, if we fire a uniform random number, 45% of such 'samples' will fall in the Y-span of  $E_1$ , 45% will fall in the Y-span of  $E_2$  and 10% will fall in the Y-span of  $E_3$ . Hence such pool of samples satisfy the distribution. Hence to draw a single sample, we follow these two steps:

1. Generate a uniform random number.
2. Locate this number on the Y axis.
3. Draw a line parallel to X axis from this point till it intersect the cumulative probability distribution of the random variable. (Here it is a discrete random variable)

4. Read the sample event from X axis.

For example, if the random number is 0.5, the event is  $E_2$ .

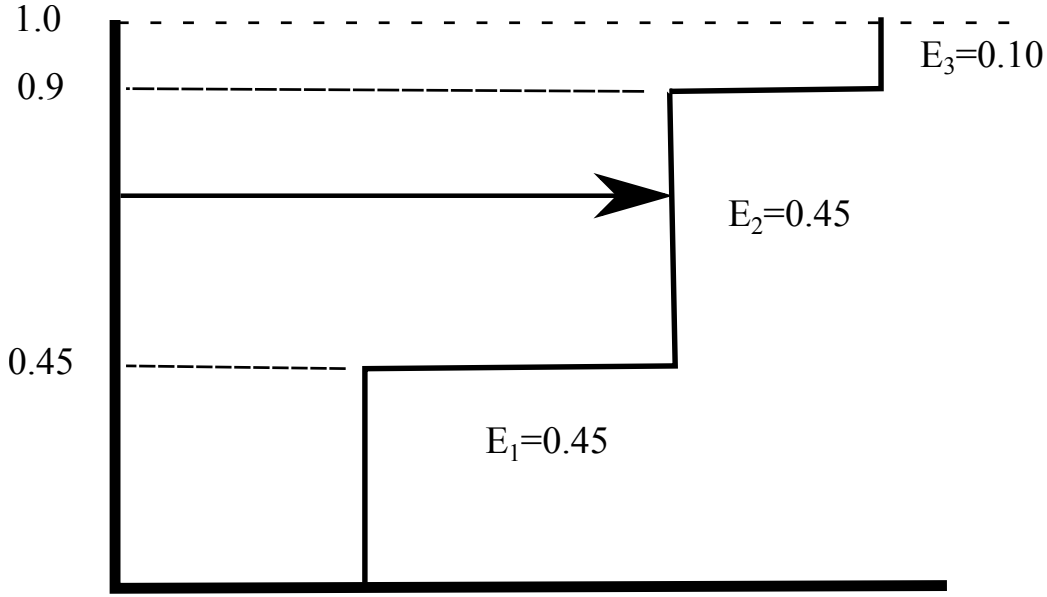


Figure 6.1: Selection of event for a discrete probability distribution

Similar procedure is used for continuous distribution as well. The logic for extending the procedure will be clear if the continuous distribution is thought as a discrete distribution with infinite fineness. Hence for any continuous probability density function, the cumulative is to be obtained first. This step is already executed for our case of IQ because we derived the cumulative ( $F_T$ ) directly. Since it is a probability distribution, it will obviously be normalized. Next step is to plot this distribution as shown in Fig. Next steps are identical to that of discrete distribution.

#### 6.4.4 Algorithm for sampling of a distribution

- Define an array where the cumulative probability of  $i$ th event is the  $i$ th member  $A$ .
- Define an event array.  $E$



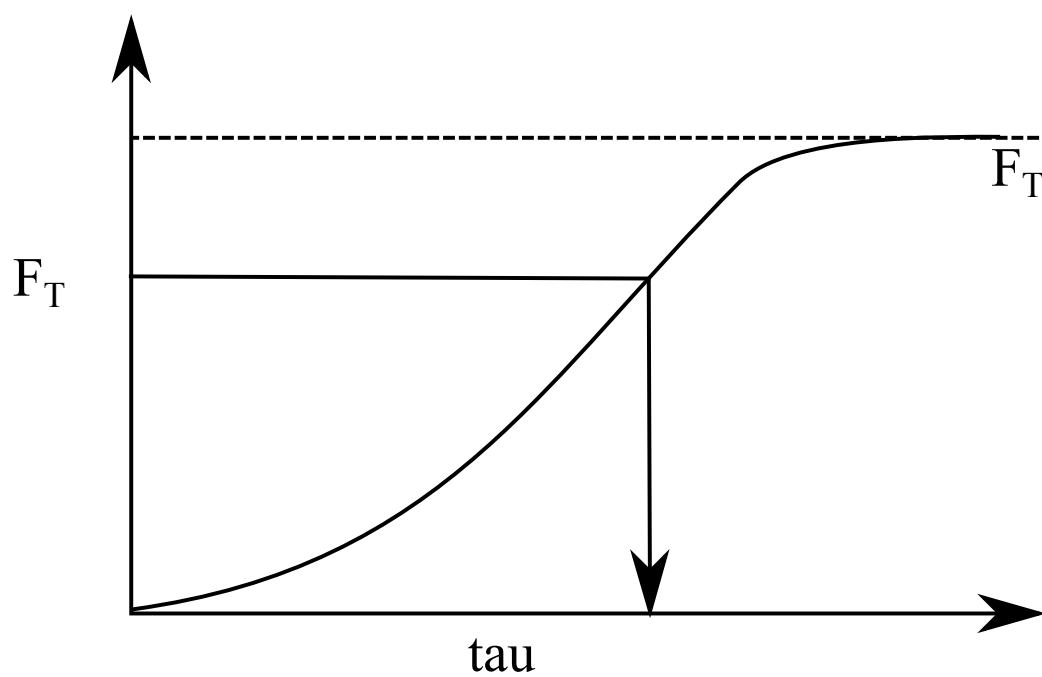


Figure 6.2: Selection of IQ: sampling from a continuous distribution

- Run a loop  $M$  times to get a sequence of  $M$  events.  
     For  $j=1, M$   
     Search for the  $j$ th event.
- Generate a random number  $\zeta$ .
- Run a loop from the beginning to end of the array:  
     for  $i = 1$  to  $N$   
     is  $\zeta < x_i$ ?  
     if yes, Event=  $i$   
     else continue
- $E(j)=i$
- End

At the end this will produce a sequence of events like 1125763221... which is a single simulation of the sequence.

**Example 6.4.1.** *Create random password using random numbers.*

*Solution:* First generate a random number

□

### 6.4.5 Implementing the changes in the system

Once the IQ is selected, the system clock is advanced by this time and the event must be executed. If the system has 3 particles which of them would break? Since it is stochastic simulation, let us talk about probability rather than certainty. Do we know anything about relative probability of breakage of these particles? Since we have knowledge of breakage rate, which is often a function of size, we may derive the relative probability from this. If the breakage rate is proportional to size (i.e.  $\Gamma(x) = kx$ ) and probability is proportional to breakage rate, the breakage probability of these three particles can be written as:  $BP1 : BP2 : BP3 :: x_1 : x_2 : x_3$ . If the size of these particles are 9, 9 and 2 respectively, the probability becomes:  $\frac{9}{9+9+5} = 0.391$ ,  $\frac{9}{9+9+5} = 0.391$  and  $1 - 2 \times 0.391 = 0.218$  respectively. Now to select the particle which will break, we construct a cumulative similar to that shown in Fig. and generate a uniform random number. The selection is made in a similar manner.

Once the particle to be broken is selected, it is broken according to the physical process governing its breakage. The same machinery for sampling can be used to generate sample daughter sizes. This step is not needed for breakage into equal sized daughter drops. Hence the selected drop (say drop 2 in this case) is deleted from the array and two new drops half the size of drop 2 (i.e. 4.5 each) is inserted into the array. An useful convention is to insert one of the daughter drops into the place of the mother drop and adding the other drop at the end of the array. In this case the new array becomes: [ 9 4.5 2 4.5].

## 6.5 Exercise

**Exercise 6.1.** *The figure below is showing a square dart board of unit dimension. This dartboard has a circular shaded area as shown in the figure. A novice player throws dart at random to this board so that the probability that the dart falls at a place is uniform. Using Kinetic Monte Carlo simulation show that the fraction of darts that fall in the shaded area approaches a value of  $\frac{\pi}{4}$  as the number of simulation increases.*

**Exercise 6.2.** *Consider a system consisting of three particles of size 2, 5 and 7 cc respectively in a box. These particles undergo breakage. The breakage rate of individual particles observed under conditions identical to that inside the box found to be proportional to their volumes with the proportionality constant 1. i.e. the particle of volume  $v$  breaks at a rate  $v/s$ . Find out the state of the system after 3 sec.*

**Exercise 6.3.** *Consider a closed vessel at room temperature containing eight drops of exactly equal size: assume any size you prefer. At time  $t=0$ , the vessel is brought to a higher temperature so that the drops start to break into two random sized daughter drops. The average rate of breakage is a first order process with rate constant  $1E-2s^{-1}$ . Simulate the system (a single simulation) for **four time steps** using Interval of Quiescence algorithm. Show all necessary steps clearly.*

**Exercise 6.4.** *Consider a batch stirred vessel with a given volume of water and kerosene. It is known that at the hydrodynamic condition required by the process both breakage and aggregation of drops occur. After sufficient time, the particle size distribution reaches a steady state. Kinetic Monte Carlo*

*simulation is to be used to simulate this process. Draw a detailed flowsheet for the simulation and write down the pseudo code.*

**Exercise 6.5.** *Briefly describe the algorithm of Kinetic Monte Carlo simulation for pure breakage process.*



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